US007220523B2

(12) **United States Patent**
Tokarski et al.

(10) **Patent No.: US 7,220,523 B2**
(45) **Date of Patent: May 22, 2007**

(54) **BRIDGED CHARGE TRANSPORT MATERIALS HAVING TWO BICYCLIC HETEROCYCLE HYDRAZONES**

(75) Inventors: **Zbigniew Tokarski**, Woodbury, MN (US); **Nusrallah Jubran**, St. Paul, MN (US); **Ramunas Lygaitis**, Kaunas (LT); **Juozas V. Grazulevicius**, Kaunas (LT); **Edmundas Montrimas**, Vilnius (LT); **Jonas Sidaravicius**, Vilnius (LT)

(73) Assignee: **Samsung Electronics Co., Ltd.**, Suwon (KR)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 399 days.

(21) Appl. No.: **10/865,427**

(22) Filed: **Jun. 10, 2004**

(65) **Prior Publication Data**

US 2005/0277037 A1 Dec. 15, 2005

(51) **Int. Cl.**
G03G 5/06 (2006.01)

(52) **U.S. Cl.** **430/77**; 430/75; 430/76; 430/78; 430/79; 430/58.45; 430/126; 399/159; 548/131; 548/133; 549/362; 549/366

(58) **Field of Classification Search** 430/75, 430/76, 77, 78, 79, 120, 58.45; 399/159; 548/131, 133; 549/362, 363
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,278,747	A	7/1981	Myrayama et al.
4,365,014	A	12/1982	Sakai et al.
4,403,025	A	9/1983	Horie et al.
4,477,550	A	10/1984	Horie et al.
4,786,571	A	11/1988	Ueda
4,808,503	A	2/1989	Yamada et al.
4,861,692	A	8/1989	Kuroda et al.
4,910,645	A	3/1990	Jonas et al.
5,089,365	A	2/1992	Kuroda et al.
RE35,475	E	3/1997	Kuroda et al.
5,942,615	A	8/1999	Kobayashi et al.
6,066,426	A	5/2000	Mott et al.
6,083,651	A	7/2000	Kobayashi et al.
6,140,004	A	10/2000	Mott et al.
6,214,503	B1	4/2001	Gaidelis et al.
6,340,548	B1	1/2002	Jubran et al.

FOREIGN PATENT DOCUMENTS

JP	2001-166519	6/2001

OTHER PUBLICATIONS

Zong et al., "3,4-Alkylenedioxy Ring Formation Via Double Mitsunobu Reactions: An Efficient Route For The Synthesis Of 3,4-Ethylenedioxythiophene (EDOT) And 3,4-Propylenedioxythiophene (Prodot) Derivatives As Monomers For Electron-Rich Conducting Polymers," *Chemical Communications*, 2002, pp. 2498-99, the Royal Society of Chemistry, Cambridge, England, UK.

Gogte et al., "Synthesis Of Potential Anticancer Agents-I," *Tetrahydron*, 1967, vol. 23 pp. 2437-2441, Pergamon Press, Oxford, England, UK.

Gonzalo et al., "Synthesis And Electropolymerisation Of 3',4'-Bis(Alkylsulfanyl)Terthiophenes And The Significance Of The Fused Dithiin Ring In 2,5-Dithienyl-3,4-Ethylenedithiothiophene (DT-EDTT)," *J. Mater. Chem*, 2002, 12, pp. 500-510, the Royal Society of Chemistry, Cambridge, England, UK.

Groenendaal et al., "Poly(3,4-Ethylenedioxythiophene) And Its Derivatives: Past, Present, And Future," *Adv. Mater.*, 2000, 12, No. 7, pp. 481-494, Wiley-VCH Verlag.

Kim et al., "New Conducting Polymers Based On Poly(3,4-Ethylenedioxypyrrole): Synthesis, Characterization, And Properties," *Chemistry Letters*, 2004, vol. 33, No. 1, pp. 46-47, the Chemical Society of Japan.

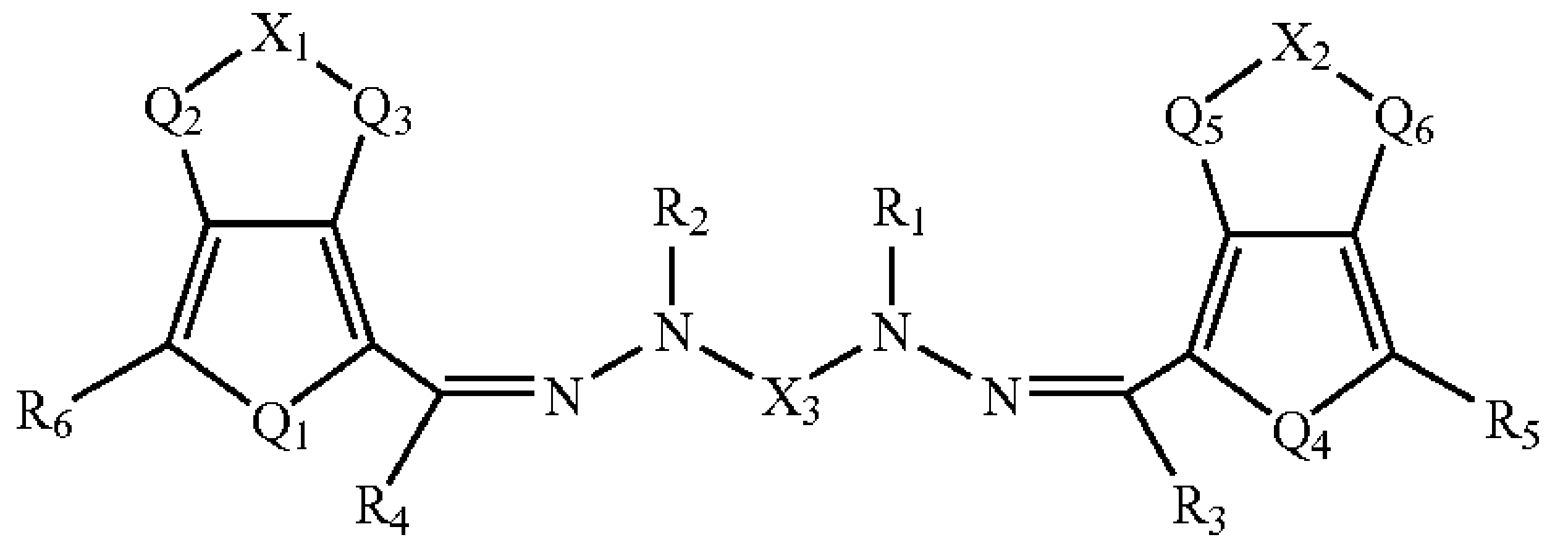
Kros et al., "Poly(3,4-Ethylenedioxythiophene)-Based Copolymers For Biosensor Applications," *J. Polymer Science: Part A: Polymer Chem.*, 2002, vol. 40, pp. 738-747, Wiley Periodicals, Inc.

Primary Examiner—Christopher RoDee
(74) *Attorney, Agent, or Firm*—Patterson Thuente Skaar & Christensen, P.A.

(57) **ABSTRACT**

Improved organophotoreceptor comprises an electrically conductive substrate and a photoconductive element on the electrically conductive substrate, the photoconductive element comprising:

(a) a charge transport material having the formula



where R_1, R_2, R_3, R_4, R_5, and R_6 comprise, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group;

X_1 and X_2 are, each independently, a —$(CH_2)_n$— group, where n is an integer between 1 and 10, inclusive;

X_3 is linking group; and

Q_1, Q_2, Q_3, Q_4, Q_5, and Q_6 are, each independently, O, S, NR, NC(=O)R' where R and R' are, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, a heterocyclic group, or an aromatic group; and

(b) a charge generating compound.

Corresponding electrophotographic apparatuses and imaging methods are described.

42 Claims, No Drawings

BRIDGED CHARGE TRANSPORT MATERIALS HAVING TWO BICYCLIC HETEROCYCLE HYDRAZONES

FIELD OF THE INVENTION

This invention relates to organophotoreceptors suitable for use in electrophotography and, more specifically, to organophotoreceptors including a charge transport material having two bicyclic heterocycle hydrazones bonded together through a linking group.

BACKGROUND OF THE INVENTION

In electrophotography, an organophotoreceptor in the form of a plate, disk, sheet, belt, drum or the like having an electrically insulating photoconductive element on an electrically conductive substrate is imaged by first uniformly electrostatically charging the surface of the photoconductive layer, and then exposing the charged surface to a pattern of light. The light exposure selectively dissipates the charge in the illuminated areas where light strikes the surface, thereby forming a pattern of charged and uncharged areas, referred to as a latent image. A liquid or solid toner is then provided in the vicinity of the latent image, and toner droplets or particles deposit in the vicinity of either the charged or uncharged areas to create a toned image on the surface of the photoconductive layer. The resulting toned image can be transferred to a suitable ultimate or intermediate receiving surface, such as paper, or the photoconductive layer can operate as an ultimate receptor for the image. The imaging process can be repeated many times to complete a single image, for example, by overlaying images of distinct color components or effect shadow images, such as overlaying images of distinct colors to form a full color final image, and/or to reproduce additional images.

Both single layer and multilayer photoconductive elements have been used. In single layer embodiments, a charge transport material and charge generating material are combined with a polymeric binder and then deposited on the electrically conductive substrate. In multilayer embodiments, the charge transport material and charge generating material are present in the element in separate layers, each of which can optionally be combined with a polymeric binder, deposited on the electrically conductive substrate. Two arrangements are possible for a two-layer photoconductive element. In one two-layer arrangement (the “dual layer” arrangement), the charge-generating layer is deposited on the electrically conductive substrate and the charge transport layer is deposited on top of the charge generating layer. In an alternate two-layer arrangement (the “inverted dual layer” arrangement), the order of the charge transport layer and charge generating layer is reversed.

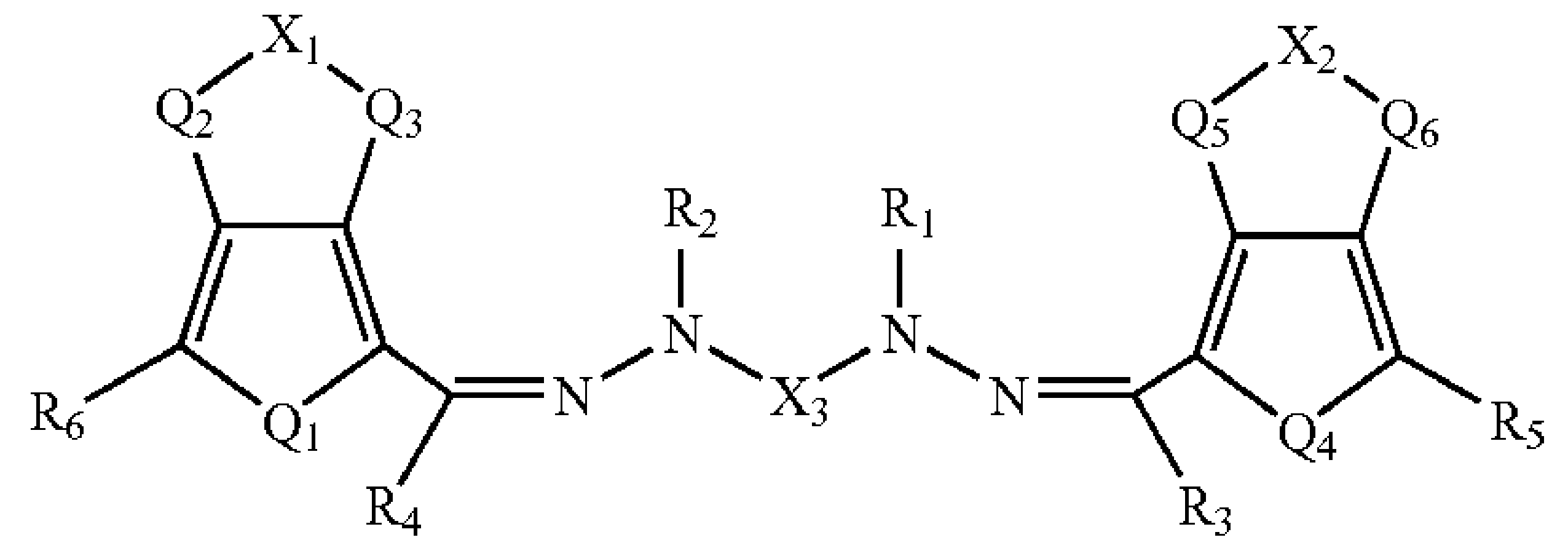
In both the single and multilayer photoconductive elements, the purpose of the charge generating material is to generate charge carriers (i.e., holes and/or electrons) upon exposure to light. The purpose of the charge transport material is to accept at least one type of these charge carriers and transport them through the charge transport layer in order to facilitate discharge of a surface charge on the photoconductive element. The charge transport material can be a charge transport compound, an electron transport compound, or a combination of both. When a charge transport compound is used, the charge transport compound accepts the hole carriers and transports them through the layer with the charge transport compound. When an electron transport compound is used, the electron transport compound accepts the electron carriers and transports them through the layer with the electron transport compound.

SUMMARY OF THE INVENTION

This invention provides organophotoreceptors having good electrostatic properties such as high V_{acc} and low V_{dis}.

In a first aspect, an organophotoreceptor comprises an electrically conductive substrate and a photoconductive element on the electrically conductive substrate, the photoconductive element comprising:

(a) a charge transport material having the formula:



(I)

where R_1, R_2, R_3, R_4, R_5, and R_6 comprise, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group;

X_1 and X_2 are, each independently, a —$(CH_2)_n$— group, where n is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C═O, O═S═O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, a SiR_eR_f group, a BR_g group, or a $P(═O)R_h$ group, where R_a, R_b, R_c, R_d, R_e, R_f, R_g, and R_h are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, an alkoxy group, an alkylsulfonyl group group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, such as cycloalkyl groups, heterocyclic groups, or a benzo group;

X_3 is linking group, such as a —$(CH_2)_m$— group, where m is an integer between 1 and 50, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C═O, O═S═O, a heterocyclic group, an aromatic group, an NR_i group, a CR_j group, a CR_kR_l group, a SiR_mR_n group, a BR_o group, or a $P(═O)R_p$ group, where R_i, R_j, R_k, R_l, R_m, R_n, R_o, and R_p are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, an alkoxy group, an alkylsulfonyl group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, such as cycloalkyl groups, heterocyclic groups, or a benzo group; and

Q_1, Q_2, Q_3, Q_4, Q_5, and Q_6 are, each independently, O, S, NR, NC(═O)R' where R and R' are, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, a heterocyclic group, or an aromatic group; and

(b) a charge generating compound.

The organophotoreceptor may be provided, for example, in the form of a plate, a flexible belt, a flexible disk, a sheet, a rigid drum, or a sheet around a rigid or compliant drum. In one embodiment, the organophotoreceptor includes: (a) a photoconductive element comprising the charge transport material, the charge generating compound, a second charge transport material, and a polymeric binder; and (b) the electrically conductive substrate.

In a second aspect, the invention features an electrophotographic imaging apparatus that comprises (a) a light imaging component; and (b) the above-described organophotoreceptor oriented to receive light from the light imaging component. The apparatus can further comprise a toner dispenser, such as a liquid toner dispenser. The method of electrophotographic imaging with photoreceptors containing the above noted charge transport materials is also described.

In a third aspect, the invention features an electrophotographic imaging process that includes (a) applying an electrical charge to a surface of the above-described organophotoreceptor; (b) imagewise exposing the surface of the organophotoreceptor to radiation to dissipate charge in selected areas and thereby form a pattern of at least relatively charged and uncharged areas on the surface; (c) contacting the surface with a toner, such as a liquid toner that includes a dispersion of colorant particles in an organic liquid, to create a toned image; and (d) transferring the toned image to a substrate.

In a fourth aspect, the invention features a charge transport material having Formula (I) above.

The invention provides suitable charge transport materials for organophotoreceptors featuring a combination of good mechanical and electrostatic properties. These photoreceptors can be used successfully with toners, such as liquid toners, to produce high quality images. The high quality of the imaging system can be maintained after repeated cycling.

Other features and advantages of the invention will be apparent from the following description of the particular embodiments thereof, and from the claims.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

An organophotoreceptor as described herein has an electrically conductive substrate and a photoconductive element including a charge generating compound and a charge transport material having two bicyclic heterocycle hydrazones bonded together through a linking group. Non-limiting examples of bicyclic heterocycles include 3,4-alkylenedioxythiophenes, 3,4-alkylenedioxyfurans, 3,4-alkylenedioxypyrroles, 3,4-alkylenedithiathiophenes, 3,4-alkylenedithiafurans, 3,4-alkylenedithiapyrroles, 3,4-alkylenediiminethiophenes, 3,4-alkylenediiminefurans, or 3,4-alkylenediiminepyrroles. These charge transport materials have desirable properties as evidenced by their performance in organophotoreceptors for electrophotography. In particular, the charge transport materials of this invention have high charge carrier mobilities and good compatibility with various binder materials, and possess excellent electrophotographic properties. The organophotoreceptors according to this invention generally have a high photosensitivity, a low residual potential, and a high stability with respect to cycle testing, crystallization, and organophotoreceptor bending and stretching. The organophotoreceptors are particularly useful in laser printers and the like as well as fax machines, photocopiers, scanners and other electronic devices based on electrophotography. The use of these charge transport materials is described in more detail below in the context of laser printer use, although their application in other devices operating by electrophotography can be generalized from the discussion below.

To produce high quality images, particularly after multiple cycles, it is desirable for the charge transport materials to form a homogeneous solution with the polymeric binder and remain approximately homogeneously distributed through the organophotoreceptor material during the cycling of the material. In addition, it is desirable to increase the amount of charge that the charge transport material can accept (indicated by a parameter known as the acceptance voltage or "V_{acc}"), and to reduce retention of that charge upon discharge (indicated by a parameter known as the discharge voltage or "V_{dis}").

The charge transport materials can be classified as a charge transport compound or an electron transport compound. There are many charge transport compounds and electron transport compounds known in the art for electrophotography. Non-limiting examples of charge transport compounds include, for example, pyrazoline derivatives, fluorene derivatives, oxadiazole derivatives, stilbene derivatives, enamine derivatives, enamine stilbene derivatives, hydrazone derivatives, carbazole hydrazone derivatives, (N,N-disubstituted)arylamines such as triaryl amines, polyvinyl carbazole, polyvinyl pyrene, polyacenaphthylene, and the charge transport compounds described in U.S. Pat. Nos. 6,689,523, 6,670,085, and 6,696,209, and U.S. patent application Ser. Nos. 10/431,135, 10/431,138, 10/699,364, 10/663,278, 10/699,581, 10/449,554, 10/748,496, 10/789,094, 10/644,547, 10/749,174, 10/749,171, 10/749,418, 10/699,039, 10/695,581, 10/692,389, 10/634,164, 10/663,970, 10/749,164, 10/772,068, 10/749,178, 10/758,869, 10/695,044, 10/772,069, 10/789,184, 10/789,077, 10/775,429, 10/775,429, 10/670,483, 10/671,255, 10/663,971, 10/760,039. All the above patents and patent applications are incorporated herein by reference.

Non-limiting examples of electron transport compounds include, for example, bromoaniline, tetracyanoethylene, tetracyanoquinodimethane, 2,4,7-trinitro-9-fluorenone, 2,4,5,7-tetranitro-9-fluorenone, 2,4,5,7-tetranitroxanthone, 2,4,8-trinitrothioxanthone, 2,6,8-trinitro-indeno[1,2-b]thiophene-4-one, and 1,3,7-trinitrodibenzo thiophene-5,5-dioxide, (2,3-diphenyl-1-indenylidene)malononitrile, 4H-thiopyran-1,1-dioxide and its derivatives such as 4-dicyanomethylene-2,6-diphenyl-4H-thiopyran-1,1-dioxide, 4-dicyanomethylene-2,6-di-m-tolyl-4H-thiopyran-1,1-dioxide, and unsymmetrically substituted 2,6-diaryl-4H-thiopyran-1,1-dioxide such as 4H-1,1-dioxo-2-(p-isopropylphenyl)-6-phenyl-4-(dicyanomethylidene)thiopyran and 4H-1,1-dioxo-2-(p-isopropylphenyl)-6-(2-thienyl)-4-(dicyanomethylidene) thiopyran, derivatives of phospha-2,5-cyclohexadiene, alkoxycarbonyl-9-fluorenylidene)malononitrile derivatives such as (4-n-butoxycarbonyl-9-fluorenylidene)malononitrile, (4-phenethoxycarbonyl-9-fluorenylidene)malononitrile, (4-carbitoxy-9-fluorenylidene)malononitrile, and diethyl(4-n-butoxycarbonyl-2,7-dinitro-9-fluorenylidene) malonate, anthraquinodimethane derivatives such as 11,11,12,12-tetracyano-2-alkylanthraquinodimethane and 11,11-dicyano-12,12-bis(ethoxycarbonyl)anthraquinodimethane, anthrone derivatives such as 1-chloro-10-[bis(ethoxycarbonyl)methylene]anthrone, 1,8-dichloro-10-[bis(ethoxycarbonyl)methylene]anthrone, 1,8-dihydroxy-10-[bis(ethoxycarbonyl)methylene]anthrone, and 1-cyano-10-[bis(ethoxycarbonyl)methylene)anthrone, 7-nitro-2-aza-9-fluroenylidene-malononitrile, diphenoquinone derivatives, benzoquinone derivatives, naphtoquinone derivatives, quinine derivatives, tetracyanoethylenecyanoethylene, 2,4,8-trinitro thioxantone, dinitrobenzene derivatives, dinitroanthracene derivatives, dinitroacridine derivatives, nitroanthraquinone derivatives, dinitroanthraquinone derivatives, succinic anhydride, maleic anhydride, dibromo maleic anhydride, pyrene derivatives, carbazole derivatives, hydrazone derivatives, N,N-dialkylaniline derivatives, diphenylamine derivatives, triphenylamine derivatives, triphenylmethane derivatives, tetracyano quinodimethane, 2,4,5,7-tetranitro-9-fluorenone, 2,4,7-trinitro-9-dicyanomethylene fluorenone, 2,4,5,7-tetranitroxanthone derivatives, 2,4,8-trinitrothioxanthone derivatives, 1,4,5,8-naphthalene bis-dicarboximide derivatives as described in U.S. Pat. Nos. 5,232,800, 4,468,444, and 4,442,193 and phenylazoquinolide derivatives as described in U.S. Pat. No. 6,472,514. In some embodiments of interest, the electron transport compound comprises an (alkoxycarbonyl-9-fluorenylidene)malononitrile derivative, such as (4-n-butoxycarbonyl-9-fluorenylidene)malononitrile, and 1,4,5,8-naphthalene bis-dicarboximide derivatives.

Although there are many charge transport materials available, there is a need for other charge transport materials to meet the various requirements of particular electrophotography applications.

In electrophotography applications, a charge-generating compound within an organophotoreceptor absorbs light to form electron-hole pairs. These electrons and holes can be transported over an appropriate time frame under a large electric field to discharge locally a surface charge that is generating the field. The discharge of the field at a particular location results in a surface charge pattern that essentially matches the pattern drawn with the light. This charge pattern then can be used to guide toner deposition. The charge transport materials described herein are especially effective at transporting charge, and in particular holes from the electron-hole pairs formed by the charge generating compound. In some embodiments, a specific electron transport compound or charge transport compound can also be used along with the charge transport material of this invention.

The layer or layers of materials containing the charge generating compound and the charge transport materials are within an organophotoreceptor. To print a two dimensional image using the organophotoreceptor, the organophotoreceptor has a two dimensional surface for forming at least a portion of the image. The imaging process then continues by cycling the organophotoreceptor to complete the formation of the entire image and/or for the processing of subsequent images.

The organophotoreceptor may be provided in the form of a plate, a flexible belt, a disk, a rigid drum, a sheet around a rigid or compliant drum, or the like. The charge transport material can be in the same layer as the charge generating compound and/or in a different layer from the charge generating compound. Additional layers can be used also, as described further below.

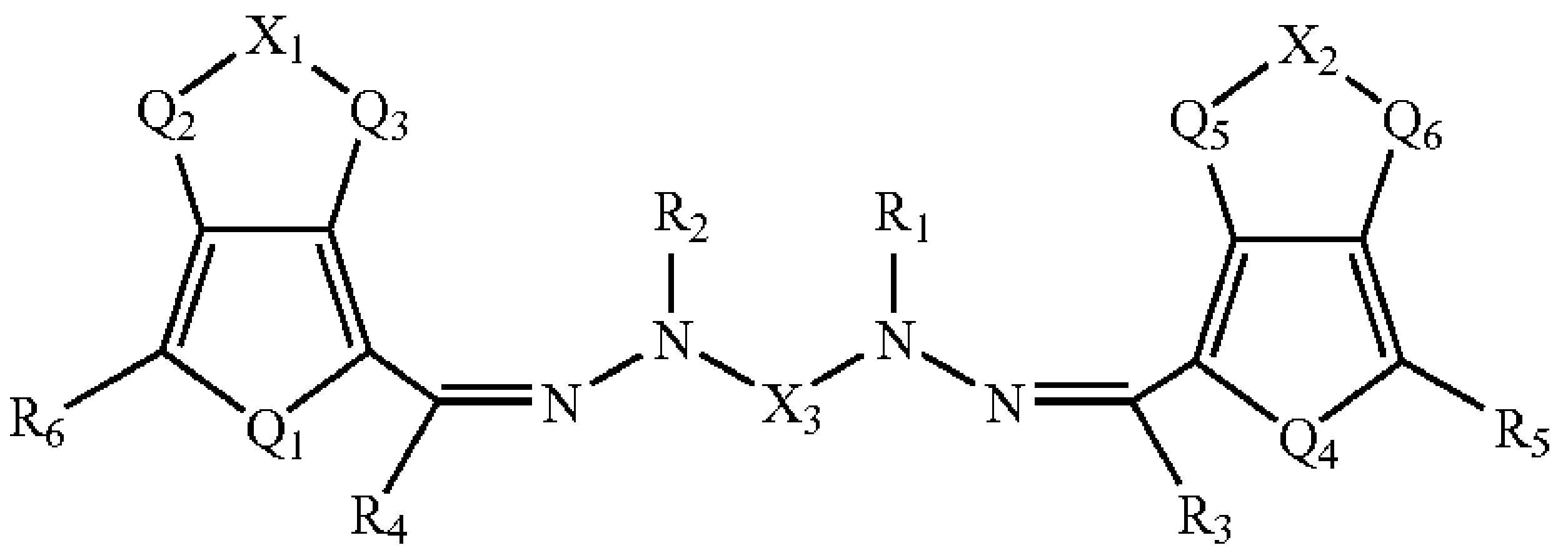
In some embodiments, the organophotoreceptor material comprises, for example: (a) a charge transport layer comprising the charge transport material and a polymeric binder; (b) a charge generating layer comprising the charge generating compound and a polymeric binder; and (c) the electrically conductive substrate. The charge transport layer may be intermediate between the charge generating layer and the electrically conductive substrate. Alternatively, the charge generating layer may be intermediate between the charge transport layer and the electrically conductive substrate. In further embodiments, the organophotoreceptor material has a single layer with both a charge transport material and a charge generating compound within a polymeric binder.

The organophotoreceptors can be incorporated into an electrophotographic imaging apparatus, such as laser printers. In these devices, an image is formed from physical embodiments and converted to a light image that is scanned onto the organophotoreceptor to form a surface latent image. The surface latent image can be used to attract toner onto the surface of the organophotoreceptor, in which the toner image is the same or the negative of the light image projected onto the organophotoreceptor. The toner can be a liquid toner or a dry toner. The toner is subsequently transferred, from the surface of the organophotoreceptor, to a receiving surface, such as a sheet of paper. After the transfer of the toner, the surface is discharged, and the material is ready to cycle again. The imaging apparatus can further comprise, for example, a plurality of support rollers for transporting a paper receiving medium and/or for movement of the photoreceptor, a light imaging component with suitable optics to form the light image, a light source, such as a laser, a toner source and delivery system and an appropriate control system.

An electrophotographic imaging process generally can comprise (a) applying an electrical charge to a surface of the above-described organophotoreceptor; (b) imagewise exposing the surface of the organophotoreceptor to radiation to dissipate charge in selected areas and thereby form a pattern of charged and uncharged areas on the surface; (c) exposing the surface with a toner, such as a liquid toner that includes a dispersion of colorant particles in an organic liquid to create a toner image, to attract toner to the charged or discharged regions of the organophotoreceptor; and (d) transferring the toner image to a substrate.

As described herein, an organophotoreceptor comprises a charge transport material having the formula:

(I)



where R_1, R_2, R_3, R_4, R_5, and R_6 comprise, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group;

X_1 and X_2 are, each independently, a $—(CH_2)_n—$ group, where n is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C═O, O═S═O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, a SiR_eR_f group, a BR_g group, or a $P(═O)R_h$ group, where R_a, R_b, R_c, R_d, R_e, R_f, R_g, and R_h are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, an alkoxy group, an alkylsulfonyl group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, such as cycloalkyl groups, heterocyclic groups, or a benzo group;

X_3 is linking group, such as a $—(CH_2)_m—$ group, where m is an integer between 1 and 50, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C═O, O═S═O, a heterocyclic group, an aromatic group, an NR_i group, a CR_j group, a CR_kR_l group, a SiR_mR_n group, a BR_o group, or a $P(═O)R_p$ group, where R_i, R_j, R_k, R_l, R_m, R_n, R_o, and R_p are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, an alkoxy group, an alkylsulfonyl group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, such as cycloalkyl groups, heterocyclic groups, or a benzo group; and

Q_1, Q_2, Q_3, Q_4, Q_5, and Q_6 are, each independently, O, S, NR, NC(=O)R' where R and R' are, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, a heterocyclic group, or an aromatic group.

A heterocyclic group includes any monocyclic or polycyclic (e.g., bicyclic, tricyclic, etc.) ring compound having at least a heteroatom (e.g., O, S, N, P, B, Si, etc.) in the ring.

An aromatic group can be any conjugated ring system containing 4n+2 pi-electrons. There are many criteria available for determining aromaticity. A widely employed criterion for the quantitative assessment of aromaticity is the resonance energy. Specifically, an aromatic group has a resonance energy. In some embodiments, the resonance energy of the aromatic group is at least 10 KJ/mol. In further embodiments, the resonance energy of the aromatic group is greater than 0.1 KJ/mol. Aromatic groups may be classified as an aromatic heterocyclic group which contains at least a heteroatom in the 4n+2 pi-electron ring, or as an aryl group which does not contain a heteroatom in the 4n+2 pi-electron ring. The aromatic group may comprise a combination of aromatic heterocyclic group and aryl group. Nonetheless, either the aromatic heterocyclic or the aryl group may have at least one heteroatom in a substituent attached to the 4n+2 pi-electron ring. Furthermore, either the aromatic heterocyclic or the aryl group may comprise a monocyclic or polycyclic (such as bicyclic, tricyclic, etc.) ring.

Non-limiting examples of the aromatic heterocyclic group are furanyl, thiophenyl, pyrrolyl, indolyl, carbazolyl, benzofuranyl, benzothiophenyl, dibenzofuranyl, dibenzothiophenyl, pyridinyl, pyridazinyl, pyrimidinyl, pyrazinyl, triazinyl, tetrazinyl, petazinyl, quinolinyl, isoquinolinyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, naphthyridinyl, acridinyl, phenanthridinyl, phenanthrolinyl, anthyridinyl, purinyl, pteridinyl, alloxazinyl, phenazinyl, phenothiazinyl, phenoxazinyl, phenoxathiinyl, dibenzo(1,4)dioxinyl, thianthrenyl, and a combination thereof. The aromatic heterocyclic group may also include any combination of the above aromatic heterocyclic groups bonded together either by a bond (as in bicarbazolyl) or by a linking group (as in 1,6di(10H-10-phenothiazinyl)hexane). The linking group may include an aliphatic group, an aromatic group, a heterocyclic group, or a combination thereof. Furthermore, the linking group may comprise at least one heteroatom such as O, S, Si, and N.

Non-limiting examples of the aryl group are phenyl, naphthyl, benzyl, or tolanyl group, sexiphenylene, phenanthrenyl, anthracenyl, coronenyl, and tolanylphenyl. The aryl group may also include any combination of the above aryl groups bonded together either by a bond (as in biphenyl group) or a linking group (as in stilbenyl, diphenyl sulfone, an arylamine group). The linking group may include an aliphatic group, an aromatic group, a heterocyclic group, or a combination thereof. Furthermore, the linking group may comprise at least one heteroatom such as O, S, Si, and N.

Substitution is liberally allowed on the chemical groups to affect various physical effects on the properties of the compounds, such as mobility, sensitivity, solubility, stability, and the like, as is known generally in the art. In the description of chemical substituents, there are certain practices common to the art that are reflected in the use of language. The term group indicates that the generically recited chemical entity (e.g., alkyl group, alkenyl group, alkynyl group, phenyl group, aromatic group, heterocyclic group, etc.) may have any substituent thereon which is consistent with the bond structure of that group. For example, where the term ‘alkyl group’ or ‘alkenyl group’ is used, that term would not only include unsubstituted linear, branched and cyclic alkyl group or alkenyl group, such as methyl, ethyl, ethenyl or vinyl, isopropyl, tert-butyl, cyclohexyl, cyclohexenyl, dodecyl and the like, but also substituents having heteroatom(s), such as 3-ethoxylpropyl, 4-(N,N-diethylamino)butyl, 3-hydroxypentyl, 2-thiolhexyl, 1,2,3-tribromoopropyl, and the like, and aromatic group, such as phenyl, naphthyl, carbazolyl, pyrrole, and the like. However, as is consistent with such nomenclature, no substitution would be included within the term that would alter the fundamental bond structure of the underlying group. For example, where a phenyl group is recited, substitution such as 2- or 4-aminophenyl, 2- or 4-(N,N-disubstituted)aminophenyl, 2,4-dihydroxyphenyl, 2,4,6-trithiophenyl, 2,4,6-trimethoxyphenyl and the like would be acceptable within the terminology, while substitution of 1,1,2,2,3,3-hexamethylphenyl would not be acceptable as that substitution would require the ring bond structure of the phenyl group to be altered to a non-aromatic form. Where the term moiety is used, such as alkyl moiety or phenyl moiety, that terminology indicates that the chemical material is not substituted. Where the term alkyl moiety is used, that term represents only an unsubstituted alkyl hydrocarbon group, whether branched, straight chain, or cyclic.

Organophotoreceptors

The organophotoreceptor may be, for example, in the form of a plate, a sheet, a flexible belt, a disk, a rigid drum, or a sheet around a rigid or compliant drum, with flexible belts and rigid drums generally being used in commercial embodiments. The organophotoreceptor may comprise, for example, an electrically conductive substrate and on the electrically conductive substrate a photoconductive element in the form of one or more layers. The photoconductive element can comprise both a charge transport material and a charge generating compound in a polymeric binder, which may or may not be in the same layer, as well as a second charge transport material such as a charge transport compound or an electron transport compound in some embodiments. For example, the charge transport material and the charge generating compound can be in a single layer. In other embodiments, however, the photoconductive element comprises a bilayer construction featuring a charge generating layer and a separate charge transport layer. The charge generating layer may be located intermediate between the electrically conductive substrate and the charge transport layer. Alternatively, the photoconductive element may have a structure in which the charge transport layer is intermediate between the electrically conductive substrate and the charge generating layer.

The electrically conductive substrate may be flexible, for example in the form of a flexible web or a belt, or inflexible, for example in the form of a drum. A drum can have a hollow cylindrical structure that provides for attachment of the drum to a drive that rotates the drum during the imaging process. Typically, a flexible electrically conductive substrate comprises an electrically insulating substrate and a thin layer of electrically conductive material onto which the photoconductive material is applied.

The electrically insulating substrate may be paper or a film forming polymer such as polyester (e.g., poly(ethylene terephthalate) or poly(ethylene naphthalate), polyimide, polysulfone, polypropylene, nylon, polyester, polycarbonate, polyvinyl resin, poly(vinyl fluoride), polystyrene and the like. Specific examples of polymers for supporting substrates included, for example, polyethersulfone (STABAR™ S-100, available from ICI), poly(vinyl fluoride) (Tedlar®, available from E.I. DuPont de Nemours & Company), poly(bisphenol-A polycarbonate) (MAKROFOL™, available from Mobay Chemical Company) and amorphous poly(ethylene terephthalate) (MELINAR™, available from ICI Americas, Inc.). The electrically conductive materials may be graphite, dispersed carbon black, iodine, conductive polymers such as polypyrroles and CALGON® conductive polymer 261 (commercially available from Calgon Corporation, Inc., Pittsburgh, Pa.), metals such as aluminum, titanium, chromium, brass, gold, copper, palladium, nickel, or stainless steel, or metal oxide such as tin oxide or indium oxide. In embodiments of particular interest, the electrically conductive material is aluminum. Generally, the photoconductor substrate has a thickness adequate to provide the required mechanical stability. For example, flexible web substrates generally have a thickness from about 0.01 to about 1 mm, while drum substrates generally have a thickness from about 0.5 mm to about 2 mm.

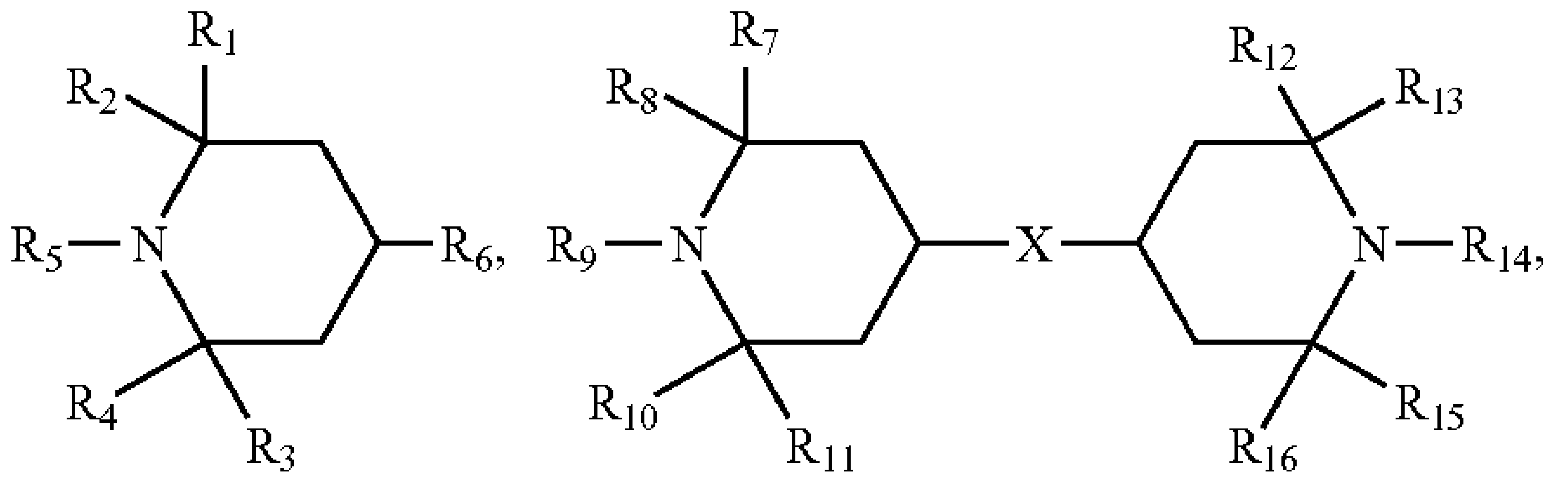
The charge generating compound is a material that is capable of absorbing light to generate charge carriers (such as a dye or pigment). Non-limiting examples of suitable charge generating compounds include, for example, metal-free phthalocyanines (e.g., ELA 8034 metal-free phthalocyanine available from H.W. Sands, Inc. or Sanyo Color Works, Ltd., CGM-X01), metal phthalocyanines such as titanium phthalocyanine, copper phthalocyanine, oxytitanium phthalocyanine (also referred to as titanyl oxyphthalocyanine, and including any crystalline phase or mixtures of crystalline phases that can act as a charge generating compound), hydroxygallium phthalocyanine, squarylium dyes and pigments, hydroxy-substituted squarylium pigments, perylimides, polynuclear quinones available from Allied Chemical Corporation under the trade name INDOFAST™ Double Scarlet, INDOFAST™ Violet Lake B, INDOFAST™ Brilliant Scarlet and INDOFAST™ Orange, quinacridones available from DuPont under the trade name MONASTRAL™ Red, MONASTRAL™ Violet and MONASTRAL™ Red Y, naphthalene 1,4,5,8-tetracarboxylic acid derived pigments including the perinones, tetrabenzoporphyrins and tetranaphthaloporphyrins, indigo- and thioindigo dyes, benzothioxanthene-derivatives, perylene 3,4,9,10-tetracarboxylic acid derived pigments, polyazo-pigments including bisazo-, trisazo- and tetrakisazo-pigments, polymethine dyes, dyes containing quinazoline groups, tertiary amines, amorphous selenium, selenium alloys such as selenium-tellurium, selenium-tellurium-arsenic and selenium-arsenic, cadmium sulphoselenide, cadmium selenide, cadmium sulphide, and mixtures thereof. For some embodiments, the charge generating compound comprises oxytitanium phthalocyanine (e.g., any phase thereof), hydroxygallium phthalocyanine or a combination thereof.

The photoconductive layer of this invention may optionally contain a second charge transport material which may be a charge transport compound, an electron transport compound, or a combination of both. Generally, any charge transport compound or electron transport compound known in the art can be used as the second charge transport material.

An electron transport compound and a UV light stabilizer can have a synergistic relationship for providing desired electron flow within the photoconductor. The presence of the UV light stabilizers alters the electron transport properties of the electron transport compounds to improve the electron transporting properties of the composite. UV light stabilizers can be ultraviolet light absorbers or ultraviolet light inhibitors that trap free radicals.

UV light absorbers can absorb ultraviolet radiation and dissipate it as heat. UV light inhibitors are thought to trap free radicals generated by the ultraviolet light and after trapping of the free radicals, subsequently to regenerate active stabilizer moieties with energy dissipation. In view of the synergistic relationship of the UV stabilizers with electron transport compounds, the particular advantages of the UV stabilizers may not be their UV stabilizing abilities, although the UV stabilizing ability may be further advantageous in reducing degradation of the organophotoreceptor over time. The improved synergistic performance of organophotoreceptors with layers comprising both an electron transport compound and a UV stabilizer are described further in copending U.S. patent application Ser. No. 10/425,333 filed on Apr. 28, 2003 to Zhu, entitled “Organophotoreceptor With A Light Stabilizer,” incorporated herein by reference.

Non-limiting examples of suitable light stabilizer include, for example, hindered trialkylamines such as TINUVIN® 144 and TINUVIN® 292 (from Ciba Specialty Chemicals, Terrytown, N.Y.), hindered alkoxydialkylamines such as TINUVIN® 123 (from Ciba Specialty Chemicals), benzotriazoles such as TINUVIN® 328, TINUVIN® 900 and TINUVIN® 928 (from Ciba Specialty Chemicals), benzophenones such as SANDUVOR® 3041 (from Clariant Corp., Charlotte, N.C.), nickel compounds such as ARBESTAB™ (from Robinson Brothers Ltd, West Midlands, Great Britain), salicylates, cyanocinnamates, benzylidene malonates, benzoates, oxanilides such as SADUVOR® VSU (from Clariant Corp., Charlotte, N.C.), triazines such as CYAGARD™ UV-1164 (from Cytec Industries Inc., N.J.), polymeric sterically hindered amines such as LUCHEM™ (from Atochem North America, Buffalo, N.Y.). In some embodiments, the light stabilizer is selected from the group consisting of hindered trialkylamines having the following formula:



where R_1, R_2, R_3, R_4, R_6, R_7, R_8, R_{10}, R_{11}, R_{12}, R_{13}, R_{14}, R_{15} are, each independently, hydrogen, alkyl group, or ester, or ether group; and R_5, R_9, and R_{14} are, each independently, alkyl group; and X is a linking group selected from the group consisting of $—O—CO—(CH_2)_m—CO—O—$ where m is between 2 to 20.

The binder generally is capable of dispersing or dissolving the charge transport material (in the case of the charge transport layer or a single layer construction), the charge generating compound (in the case of the charge generating layer or a single layer construction) and/or an electron transport compound for appropriate embodiments. Examples of suitable binders for both the charge generating layer and charge transport layer generally include, for example, poly(styrene-co-butadiene), poly(styrene-co-acrylonitrile), modified acrylic polymers, poly(vinyl acetate), styrene-alkyd resins, soya-alkyl resins, poly(vinyl chloride), poly(vinylidene chloride), polyacrylonitrile, polycarbonates, polyacrylic acid, polyacrylates, polymethacrylates, styrene polymers, poly(vinyl butyral), alkyd resins, polyamides, polyurethanes, polyesters, polysulfones, polyethers, polyketones, phenoxy resins, epoxy resins, silicone resins, polysiloxanes, poly(hydroxyether) resins, poly(hydroxystyrene) resins, novolak, poly(phenylglycidyl ether-co-dicyclopentadiene), copolymers of monomers used in the above-mentioned polymers, and combinations thereof. Specific suitable binders include, for example, poly(vinyl butyral), polycarbonate, and polyester. Non-limiting examples of poly(vinyl butyral) include BX-1 and BX-5 from Sekisui Chemical Co. Ltd., Japan. Non-limiting examples of suitable polycarbonate include polycarbonate A which is derived from bisphenol-A (e.g. IUPILON®-A from Mitsubishi Engineering Plastics, or LEXAN® 145 from General Electric); polycarbonate Z which is derived from cyclohexylidene bisphenol (e.g. IUPILON®-Z from Mitsubishi Engineering Plastics Corp, White Plain, N.Y.); and polycarbonate C which is derived from methylbisphenol A (from Mitsubishi Chemical Corporation). Non-limiting examples of suitable polyester binders include ortho-poly(ethylene terephthalate) (e.g. OPET® TR-4 from Kanebo Ltd., Yamaguchi, Japan).

Suitable optional additives for any one or more of the layers include, for example, antioxidants, coupling agents, dispersing agents, curing agents, surfactants, and combinations thereof.

The photoconductive element overall typically has a thickness from about 10 microns to about 45 microns. In the dual layer embodiments having a separate charge generating layer and a separate charge transport layer, charge generation layer generally has a thickness form about 0.5 microns to about 2 microns, and the charge transport layer has a thickness from about 5 microns to about 35 microns. In embodiments in which the charge transport material and the charge generating compound are in the same layer, the layer with the charge generating compound and the charge transport composition generally has a thickness from about 7 microns to about 30 microns. In embodiments with a distinct electron transport layer, the electron transport layer has an average thickness from about 0.5 microns to about 10 microns and in further embodiments from about 1 micron to about 3 microns. In general, an electron transport overcoat layer can increase mechanical abrasion resistance, increases resistance to carrier liquid and atmospheric moisture, and decreases degradation of the photoreceptor by corona gases. A person of ordinary skill in the art will recognize that additional ranges of thickness within the explicit ranges above are contemplated and are within the present disclosure.

Generally, for the organophotoreceptors described herein, the charge generation compound is in an amount from about 0.5 to about 25 weight percent, in further embodiments in an amount from about 1 to about 15 weight percent, and in other embodiments in an amount from about 2 to about 10 weight percent, based on the weight of the photoconductive layer. The charge transport material is in an amount from about 10 to about 80 weight percent, based on the weight of the photoconductive layer, in further embodiments in an amount from about 35 to about 60 weight percent, and in other embodiments from about 45 to about 55 weight percent, based on the weight of the photoconductive layer. The optional second charge transport material, when present, can be in an amount of at least about 2 weight percent, in other embodiments from about 2.5 to about 25 weight percent, based on the weight of the photoconductive layer, and in further embodiments in an amount from about 4 to about 20 weight percent, based on the weight of the photoconductive layer. The binder is in an amount from about 15 to about 80 weight percent, based on the weight of the photoconductive layer, and in further embodiments in an amount from about 20 to about 75 weight percent, based on the weight of the photoconductive layer. A person of ordinary skill in the art will recognize that additional ranges within the explicit ranges of compositions are contemplated and are within the present disclosure.

For the dual layer embodiments with a separate charge generating layer and a charge transport layer, the charge generation layer generally comprises a binder in an amount from about 10 to about 90 weight percent, in further embodiments from about 15 to about 80 weight percent and in some embodiments in an amount from about 20 to about 75 weight percent, based on the weight of the charge generation layer. The optional charge transport material in the charge generating layer, if present, generally can be in an amount of at least about 2.5 weight percent, in further embodiments from about 4 to about 30 weight percent and in other embodiments in an amount from about 10 to about 25 weight percent, based on the weight of the charge generating layer. The charge transport layer generally comprises a binder in an amount from about 20 weight percent to about 70 weight percent and in further embodiments in an amount from about 30 weight percent to about 50 weight percent. A person of ordinary skill in the art will recognize that additional ranges of binder concentrations for the dual layer embodiments within the explicit ranges above are contemplated and are within the present disclosure.

For the embodiments with a single layer having a charge generating compound and a charge transport material, the photoconductive layer generally comprises a binder, a charge transport material, and a charge generation compound. The charge generation compound can be in an amount from about 0.05 to about 25 weight percent and in further embodiment in an amount from about 2 to about 15 weight percent, based on the weight of the photoconductive layer. The charge transport material can be in an amount from about 10 to about 80 weight percent, in other embodiments from about 25 to about 65 weight percent, in additional embodiments from about 30 to about 60 weight percent and in further embodiments in an amount from about 35 to about 55 weight percent, based on the weight of the photoconductive layer, with the remainder of the photoconductive layer comprising the binder, and optionally additives, such as any conventional additives. A single layer with a charge transport composition and a charge generating compound generally comprises a binder in an amount from about 10 weight percent to about 75 weight percent, in other embodiments from about 20 weight percent to about 60 weight percent, and in further embodiments from about 25 weight percent to about 50 weight percent. Optionally, the layer with the charge generating compound and the charge transport material may comprise a second charge transport material. The optional second charge transport material, if present, generally can be in an amount of at least about 2.5 weight percent, in further embodiments from about 4 to about 30 weight percent and in other embodiments in an amount from about 10 to about 25 weight percent, based on the weight of the photoconductive layer. A person of ordinary skill in the art will recognize that additional composition ranges within the explicit compositions ranges for the layers above are contemplated and are within the present disclosure.

In general, any layer with an electron transport layer can advantageously further include a UV light stabilizer. In particular, the electron transport layer generally can comprise an electron transport compound, a binder, and an optional UV light stabilizer. An overcoat layer comprising an electron transport compound is described further in copending U.S. patent application Ser. No. 10/396,536 to Zhu et al. entitled, "Organophotoreceptor With An Electron Transport Layer," incorporated herein by reference. For example, an electron transport compound as described above may be used in the release layer of the photoconductors described herein. The electron transport compound in an electron transport layer can be in an amount from about 10 to about 50 weight percent, and in other embodiments in an amount from about 20 to about 40 weight percent, based on the weight of the electron transport layer. A person of ordinary skill in the art will recognize that additional ranges of compositions within the explicit ranges are contemplated and are within the present disclosure.

The UV light stabilizer, if present, in any one or more appropriate layers of the photoconductor generally is in an amount from about 0.5 to about 25 weight percent and in some embodiments in an amount from about 1 to about 10 weight percent, based on the weight of the particular layer. A person of ordinary skill in the art will recognize that additional ranges of compositions within the explicit ranges are contemplated and are within the present disclosure.

For example, the photoconductive layer may be formed by dispersing or dissolving the components, such as one or more of a charge generating compound, the charge transport material of this invention, a second charge transport material such as a charge transport compound or an electron transport compound, a UV light stabilizer, and a polymeric binder in organic solvent, coating the dispersion and/or solution on the respective underlying layer and drying the coating. In particular, the components can be dispersed by high shear homogenization, ball-milling, attritor milling, high energy bead (sand) milling or other size reduction processes or mixing means known in the art for effecting particle size reduction in forming a dispersion.

The photoreceptor may optionally have one or more additional layers as well. An additional layer can be, for example, a sub-layer or an overcoat layer, such as a barrier layer, a release layer, a protective layer, or an adhesive layer. A release layer or a protective layer may form the uppermost layer of the photoconductor element. A barrier layer may be sandwiched between the release layer and the photoconductive element or used to overcoat the photoconductive element. The barrier layer provides protection from abrasion to the underlayers. An adhesive layer locates and improves the adhesion between a photoconductive element, a barrier layer and a release layer, or any combination thereof. A sub-layer is a charge blocking layer and locates between the electrically conductive substrate and the photoconductive element. The sub-layer may also improve the adhesion between the electrically conductive substrate and the photoconductive element.

Suitable barrier layers include, for example, coatings such as crosslinkable siloxanol-colloidal silica coating and hydroxylated silsesquioxane-colloidal silica coating, and organic binders such as poly(vinyl alcohol), methyl vinyl ether/maleic anhydride copolymer, casein, poly(vinyl pyrrolidone), poly(acrylic acid), gelatin, starch, polyurethanes, polyimides, polyesters, polyamides, poly(vinyl acetate), poly(vinyl chloride), poly(vinylidene chloride), polycarbonates, poly(vinyl butyral), poly(vinyl acetoacetal), poly(vinyl formal), polyacrylonitrile, polymethylmethacrylate, polyacrylates, poly(vinyl carbazoles), copolymers of monomers used in the above-mentioned polymers, vinyl chloride/vinyl acetate/vinyl alcohol terpolymers, vinyl chloride/vinyl acetate/maleic acid terpolymers, ethylene/vinyl acetate copolymers, vinyl chloride/vinylidene chloride copolymers, cellulose polymers, and mixtures thereof. The above barrier layer polymers optionally may contain small inorganic particles such as fumed silica, silica, titania, alumina, zirconia, or a combination thereof. Barrier layers are described further in U.S. Pat. No. 6,001,522 to Woo et al., entitled "Barrier Layer For Photoconductor Elements Comprising An Organic Polymer And Silica," incorporated herein by reference. The release layer topcoat may comprise any release layer composition known in the art. In some embodiments, the release layer is a fluorinated polymer, siloxane polymer, fluorosilicone polymer, silane, polyethylene, polypropylene, polyacrylate, or a combination thereof. The release layers can comprise crosslinked polymers.

The release layer may comprise, for example, any release layer composition known in the art. In some embodiments, the release layer comprises a fluorinated polymer, siloxane polymer, fluorosilicone polymer, polysilane, polyethylene, polypropylene, polyacrylate, poly(methyl methacrylate-co-methacrylic acid), urethane resins, urethane-epoxy resins, acrylated-urethane resins, urethane-acrylic resins, or a combination thereof. In further embodiments, the release layers comprise crosslinked polymers.

The protective layer can protect the organophotoreceptor from chemical and mechanical degradation. The protective layer may comprise any protective layer composition known in the art. In some embodiments, the protective layer is a fluorinated polymer, siloxane polymer, fluorosilicone polymer, polysilane, polyethylene, polypropylene, polyacrylate, poly(methyl methacrylate-co-methacrylic acid), urethane resins, urethane-epoxy resins, acrylated-urethane resins, urethane-acrylic resins, or a combination thereof. In some embodiments of particular interest, the release layers are crosslinked polymers.

An overcoat layer may comprise an electron transport compound as described further in copending U.S. patent application Ser. No. 10/396,536, filed on Mar. 25, 2003 to Zhu et al. entitled, "Organoreceptor With An Electron Transport Layer," incorporated herein by reference. For example, an electron transport compound, as described above, may be used in the release layer of this invention. The electron transport compound in the overcoat layer can be in an amount from about 2 to about 50 weight percent, and in other embodiments in an amount from about 10 to about 40 weight percent, based on the weight of the release layer. A person of ordinary skill in the art will recognize that additional ranges of composition within the explicit ranges are contemplated and are within the present disclosure.

Generally, adhesive layers comprise a film forming polymer, such as polyester, poly(vinyl butyral), poly(vinyl pyrrolidone), polyurethane, poly(methyl methacrylate), poly (hydroxy amino ether) and the like. Barrier and adhesive layers are described further in U.S. Pat. No. 6,180,305 to Ackley et al., entitled "Organic Photoreceptors for Liquid Electrophotography," incorporated herein by reference.

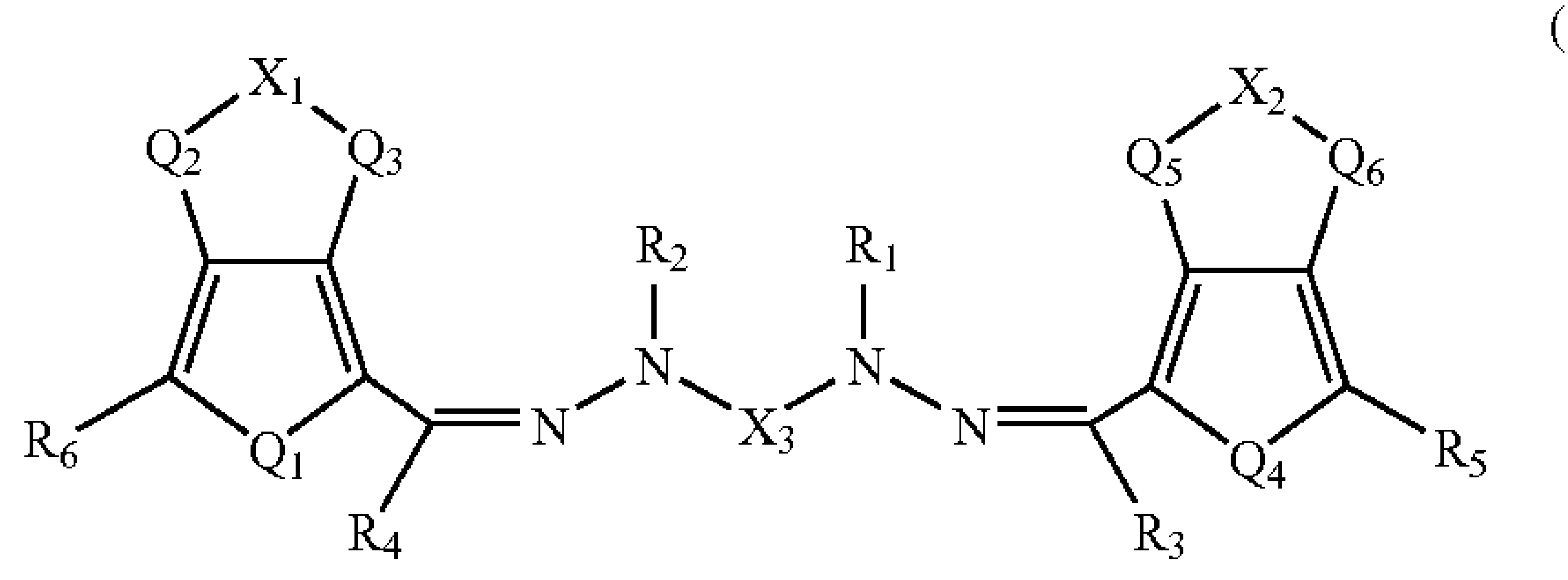
Sub-layers can comprise, for example, poly(vinyl butyral), organosilanes, hydrolyzable silanes, epoxy resins, polyesters, polyamides, polyurethanes, cellulosics and the like. In some embodiments, the sub-layer has a dry thickness between about 20 Angstroms and about 20,000 Angstroms. Sublayers containing metal oxide conductive particles can be between about 1 and about 25 microns thick. A person of ordinary skill in the art will recognize that additional ranges of compositions and thickness within the explicit ranges are contemplated and are within the present disclosure.

The charge transport materials as described herein, and photoreceptors including these compounds, are suitable for use in an imaging process with either dry or liquid toner development. For example, any dry toners and liquid toners known in the art may be used in the process and the apparatus of this invention. Liquid toner development can be desirable because it offers the advantages of providing higher resolution images and requiring lower energy for image fixing compared to dry toners. Examples of suitable liquid toners are known in the art. Liquid toners generally comprise toner particles dispersed in a carrier liquid. The toner particles can comprise a colorant/pigment, a resin binder, and/or a charge director. In some embodiments of liquid toner, a resin to pigment ratio can be from 1:1 to 10:1, and in other embodiments, from 4:1 to 8:1. Liquid toners are described further in Published U.S. Patent Applications 2002/0128349, entitled “Liquid Inks Comprising A Stable Organosol,” and 2002/0086916, entitled “Liquid Inks Comprising Treated Colorant Particles,” and U.S. Pat. No. 6,649,316, entitled “Phase Change Developer For Liquid Electrophotography,” all three of which are incorporated herein by reference.

Charge Transport Material

As described herein, an organophotoreceptor comprises a charge transport material having the formula

(I)



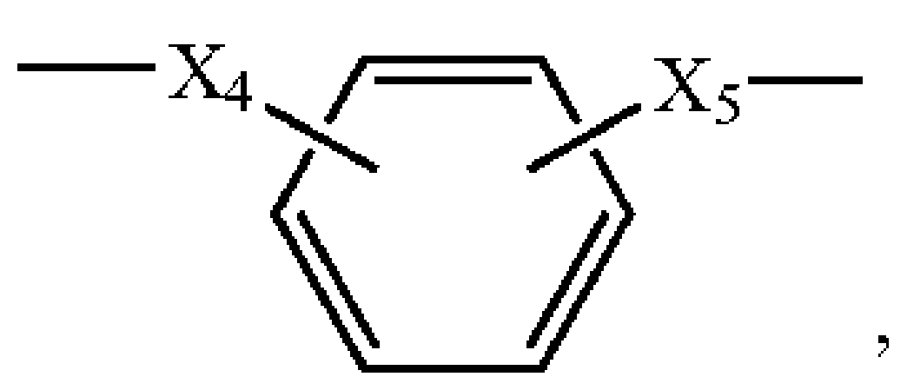
where R_1, R_2, R_3, R_4, R_5, and R_6 comprise, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group;

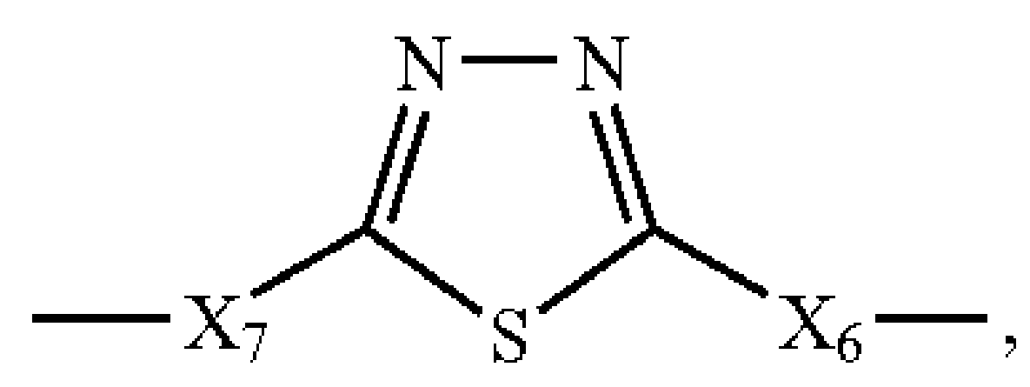
X_1 and X_2 are, each independently, a —$(CH_2)_n$— group, where n is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C═O, O═S═O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, a SiR_eR_f group, a BR_g group, or a $P(═O)R_h$ group, where R_a, R_b, R_c, R_d, R_e, R_f, R_g, and R_h are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, an alkoxy group, an alkylsulfonyl group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, such as cycloalkyl groups, heterocyclic groups, or a benzo group;

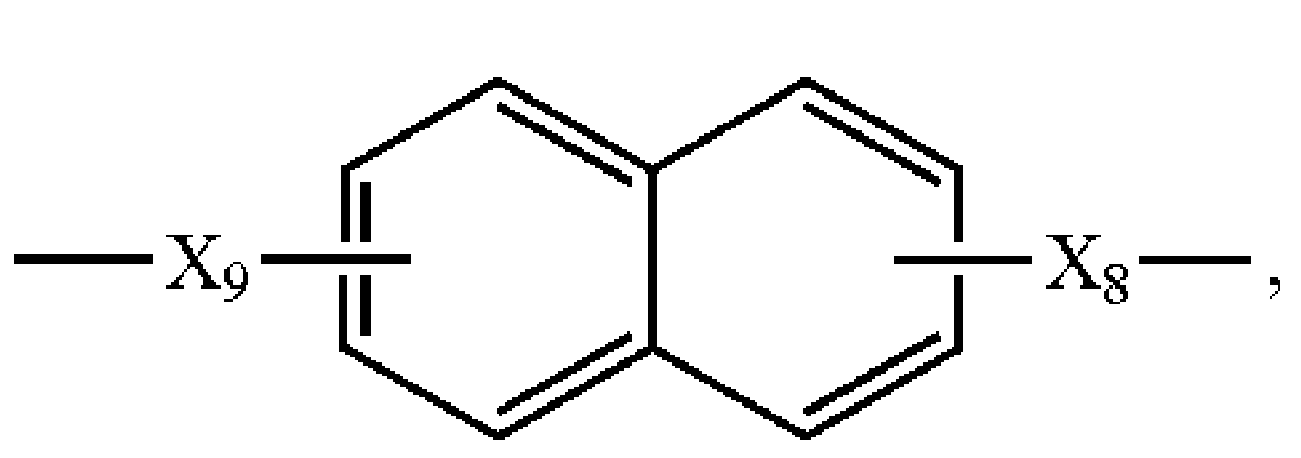
X_3 is linking group, such as a —$(CH_2)_m$— group, where m is an integer between 1 and 50, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C═O, O═S═O, a heterocyclic group, an aromatic group, an NR_i group, a CR_j group, a CR_kR_l group, a SiR_mR_n group, a BR_o group, or a $P(═O)R_p$ group, where R_i, R_j, R_k, R_l, R_m, R_n, R_o, and R_p are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, an alkoxy group, an alkylsulfonyl group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, such as cycloalkyl groups, heterocyclic groups, or a benzo group; and

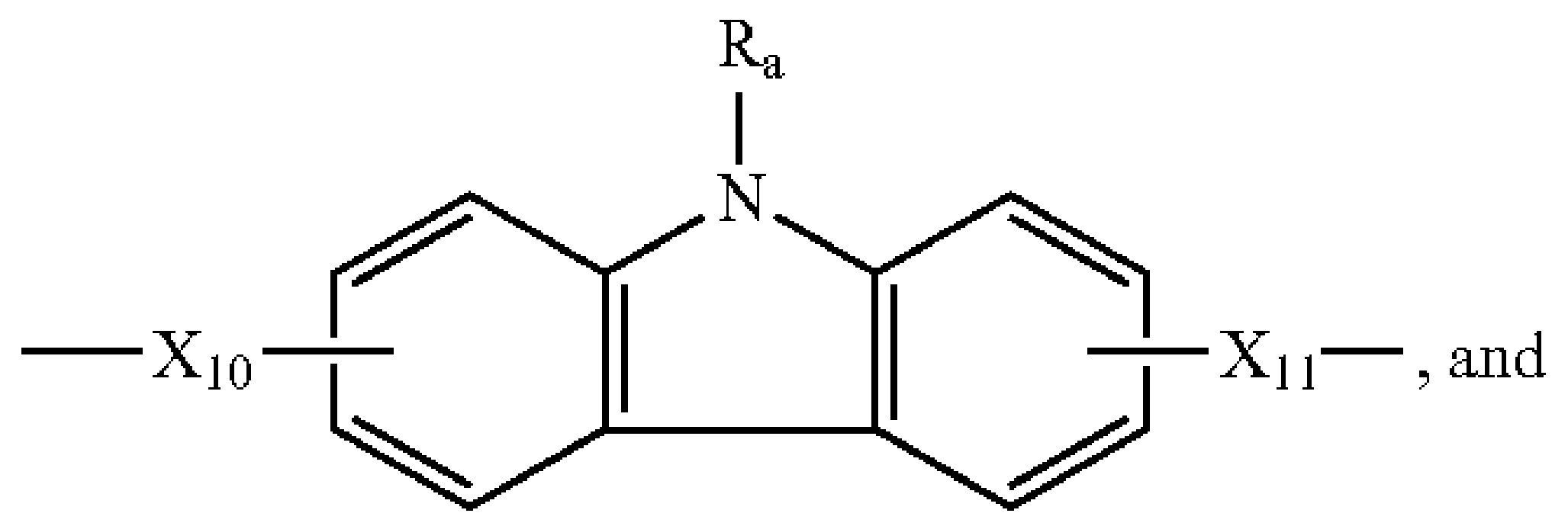
Q_1, Q_2, Q_3, Q_4, Q_5, and Q_6 are, each independently, O, S, NR, NC(═O)R' where R and R' are, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, a heterocyclic group, or an aromatic group.

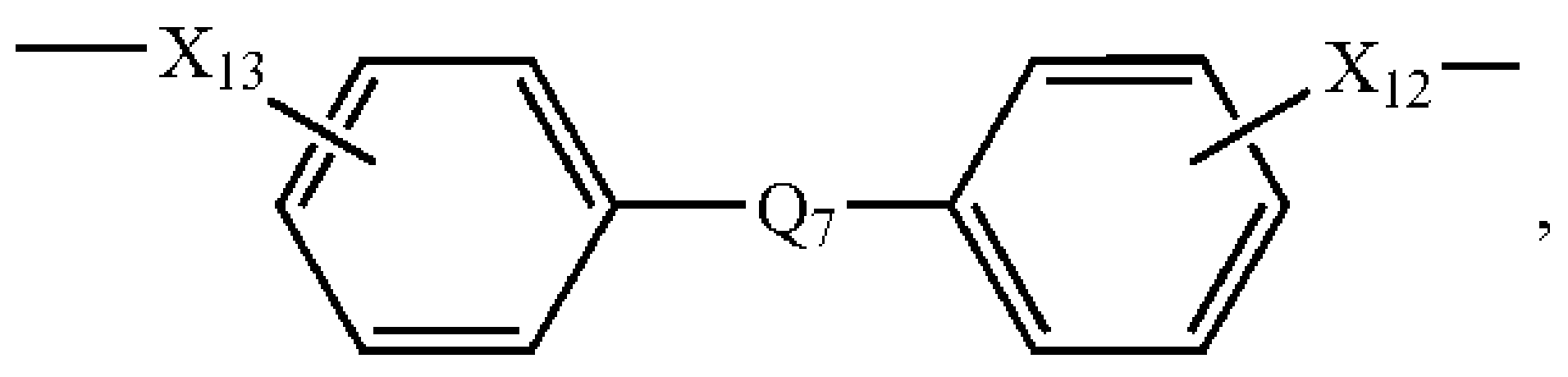
In some embodiments of interest, X_3 is selected from the group consisting of the following formulae:



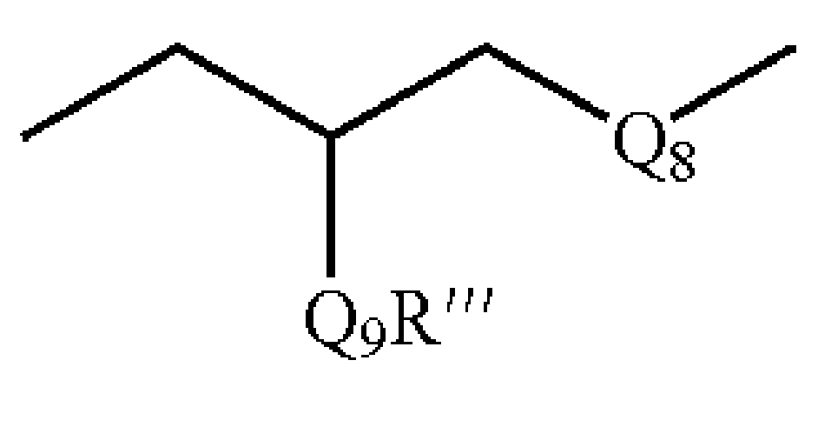






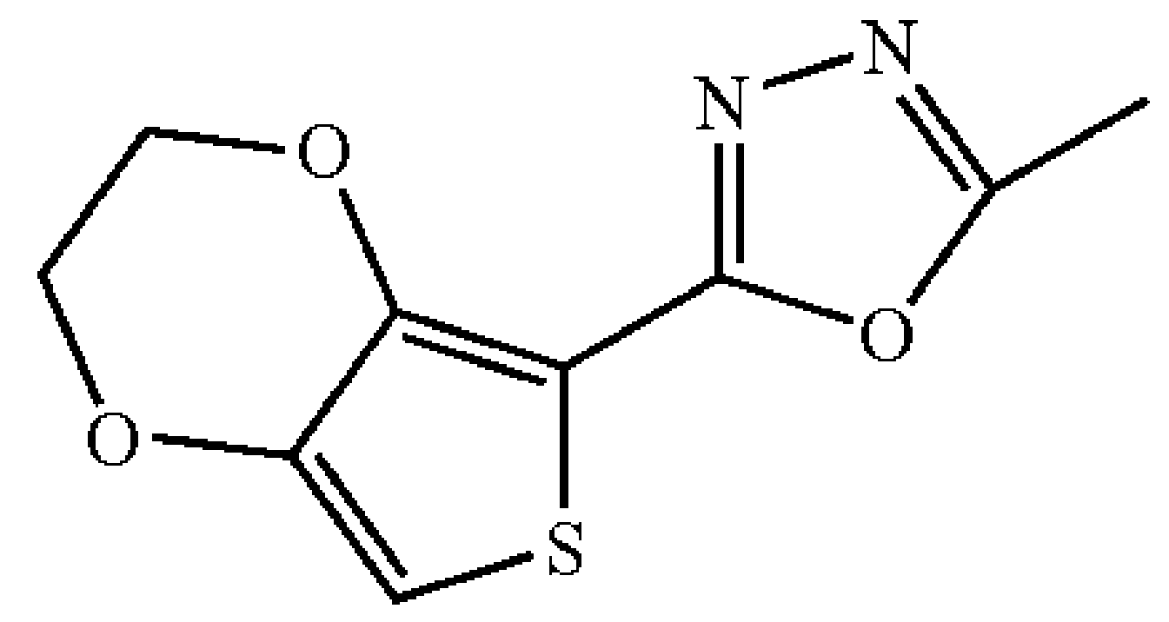


where Q_7 is a bond, O, S, C═O, SO_2, C(═O)O, an NR_b group, or a CR_cR_d group; R_a, R_b, R_c, and R_d are, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group; and X_4, X_5, X_6, X_7, X_8, X_9, X_{10}, X_{11}, X_{12}, and X_{13} are, each independently, a bond or a bridging group, such as a —$(CH_2)_p$— group, where p is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C═O, O═S═O, a heterocyclic group, an aromatic group, an NR_q group, a CR_r group, a CR_sR_t group, a SiR_uR_v group, a BR_w group, or a $P(═O)R_x$ group, where R_q, R_r, R_s, R_t, R_u, R_v, R_w, and R_x are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, an alkoxy group, an alkylsulfonyl group, an alkenyl group, such as a vinyl group, an allyl group, and a 2-phenylethenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, such as cycloalkyl groups, heterocyclic groups, or a benzo group. In further embodiments, X_4, X_5, X_6, X_7, X_8, X_9, X_{10}, X_{11}, X_{12}, and X_{13} have, each independently, the following formula:

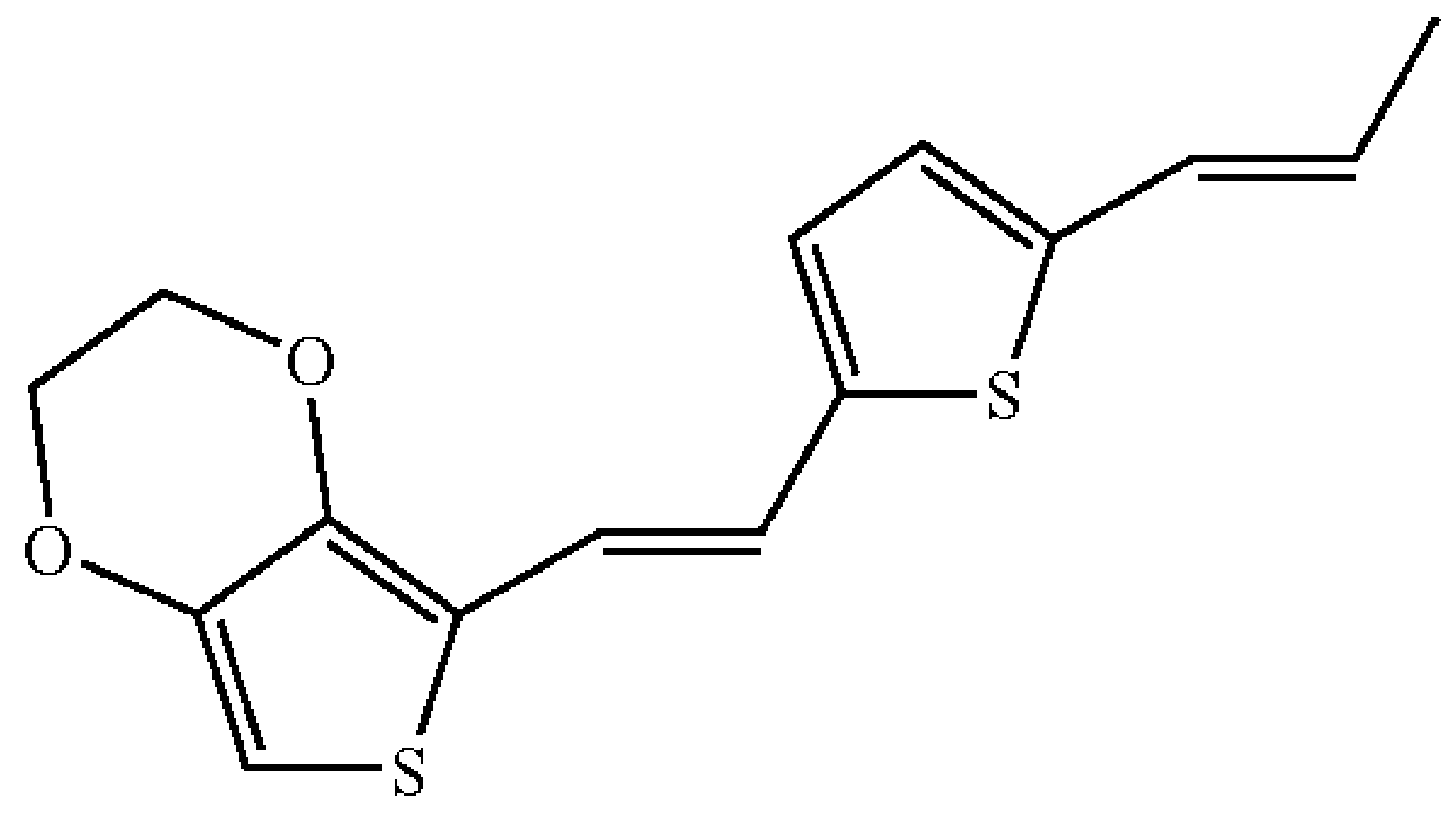


where Q_8 and Q_9 are, each independently, O, S, NR" where R" and R''' are, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, a heterocyclic group, or an aromatic group.

In other embodiments of interest, R_5 and R_6 are, each independently, selected from the group consisting of the following formulae:

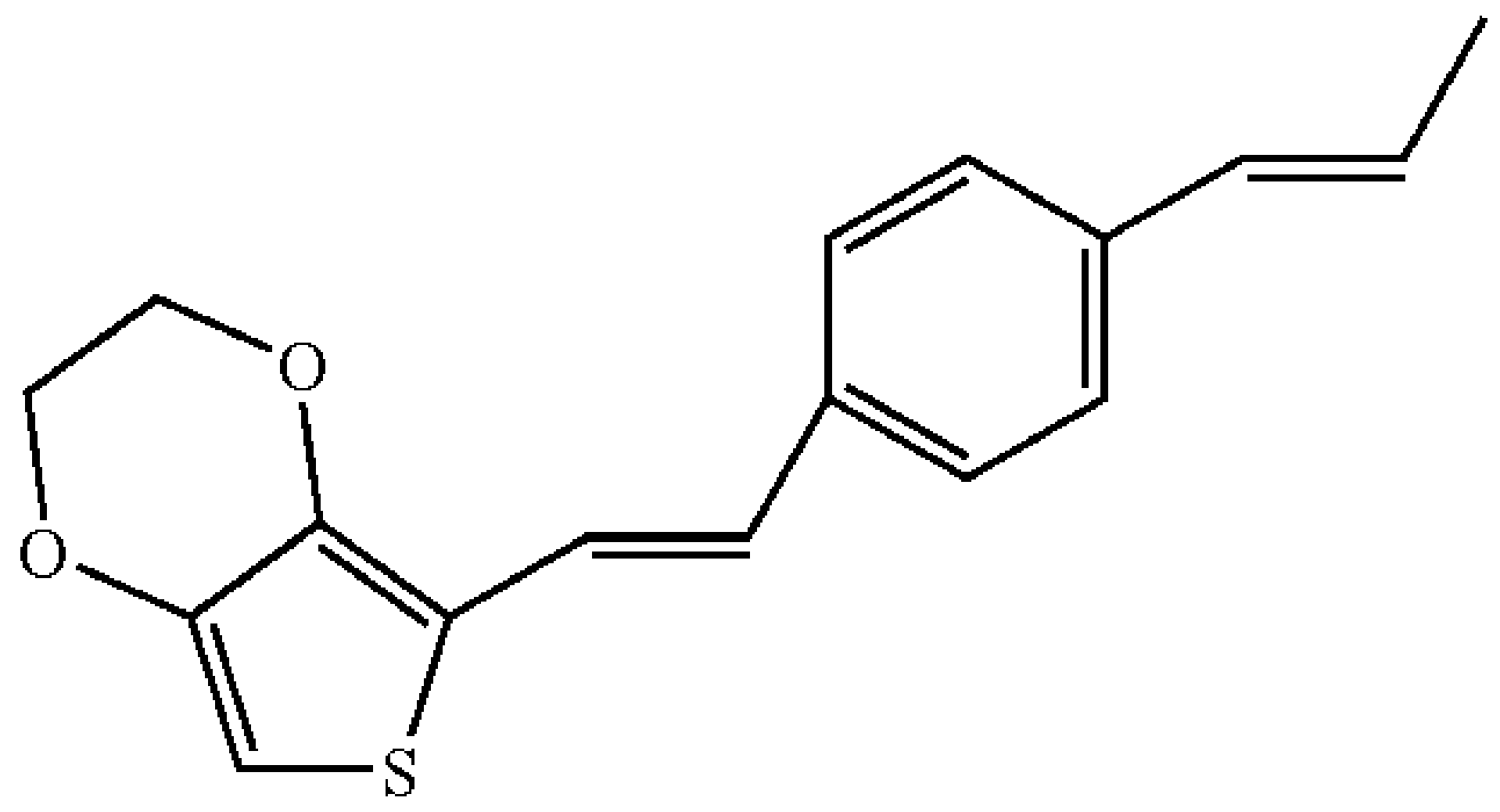


,

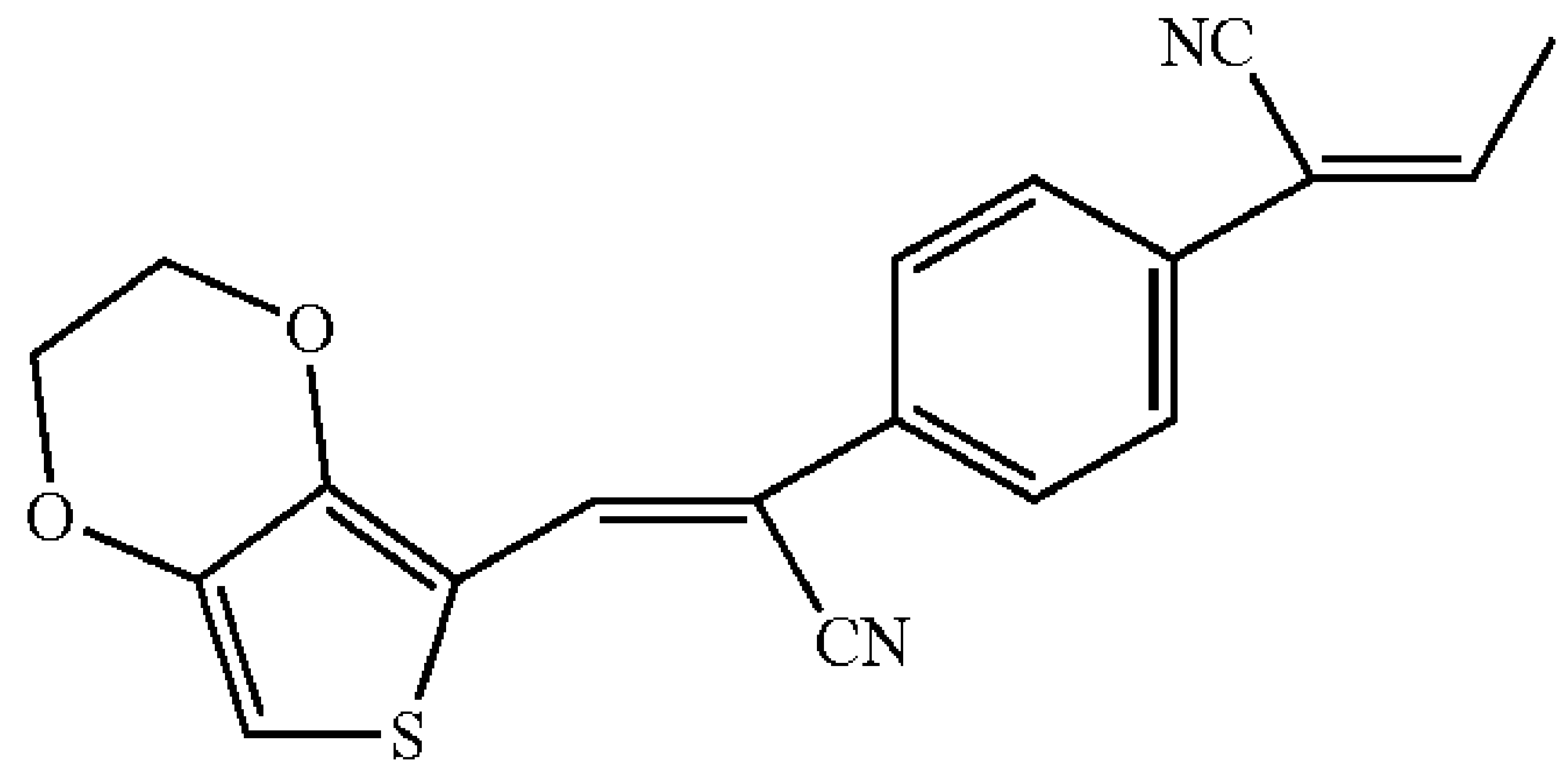


,

-continued



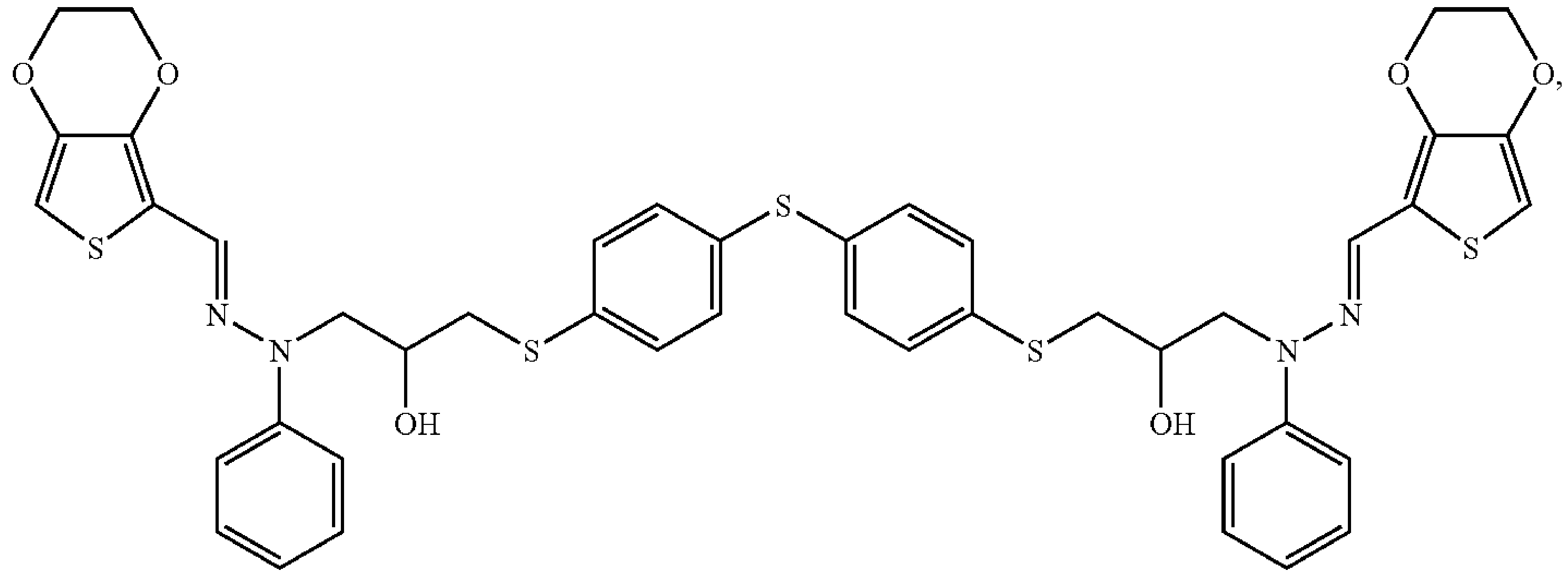
, and



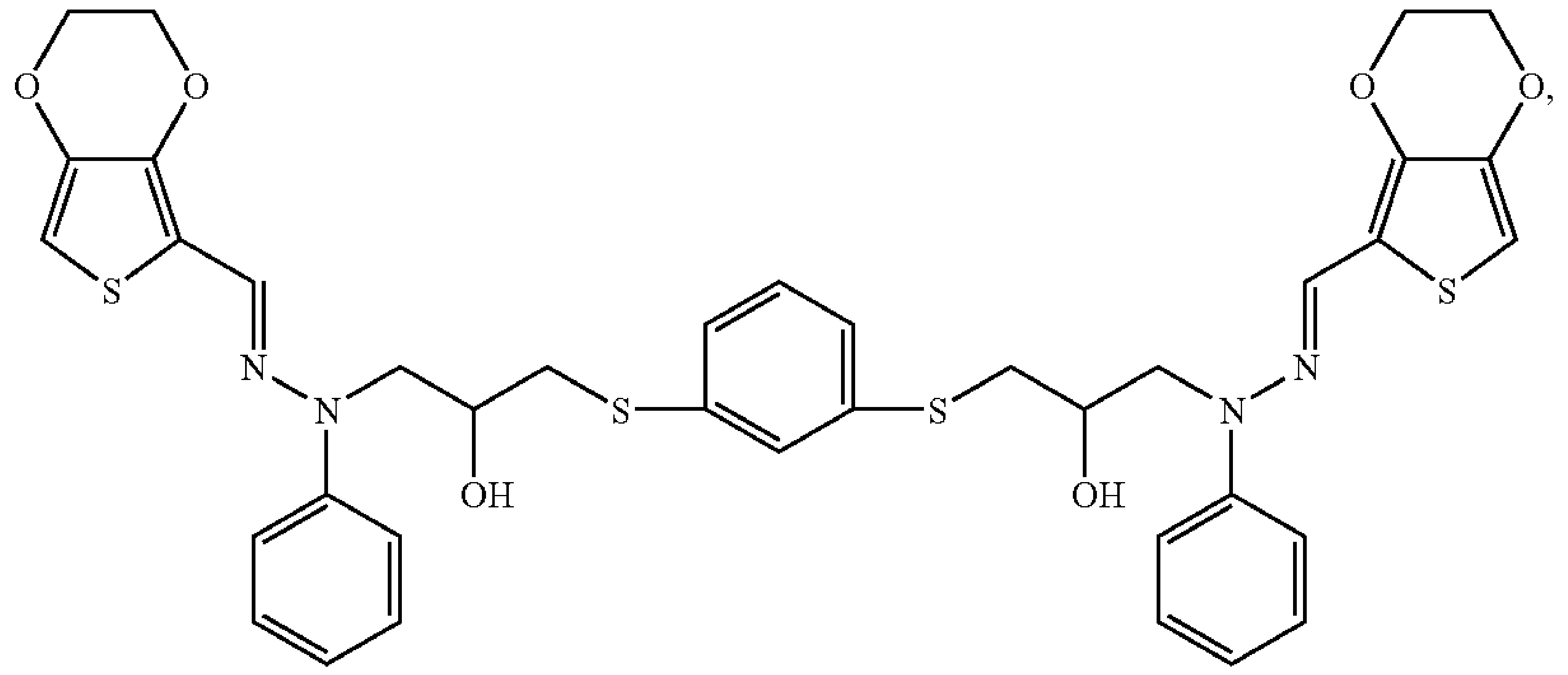
.

Specific, non-limiting examples of suitable charge transport materials within Formula (I) of the present invention have the following structures:

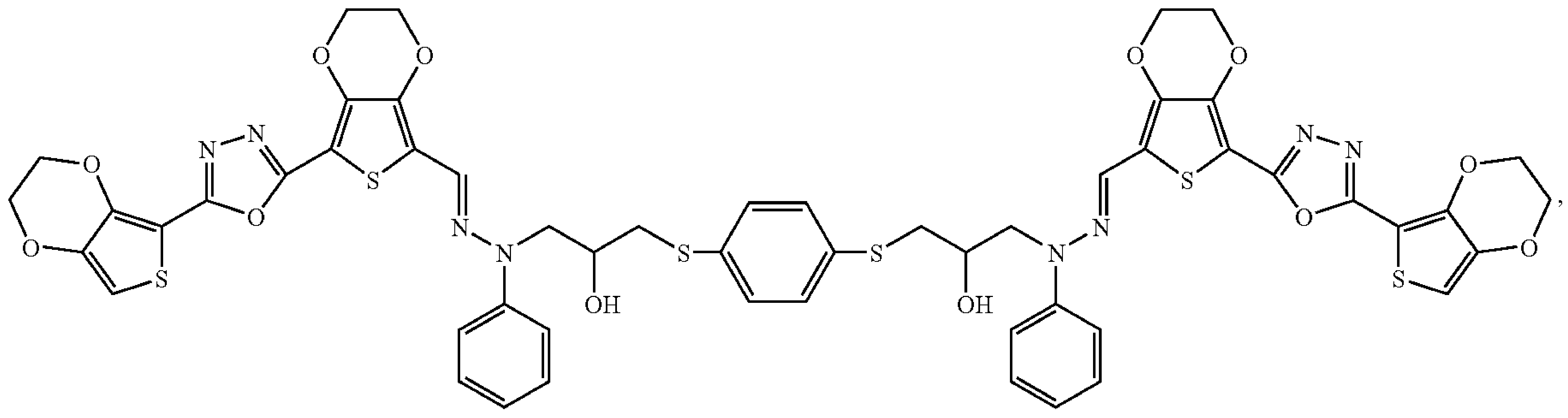
(1)



(2)

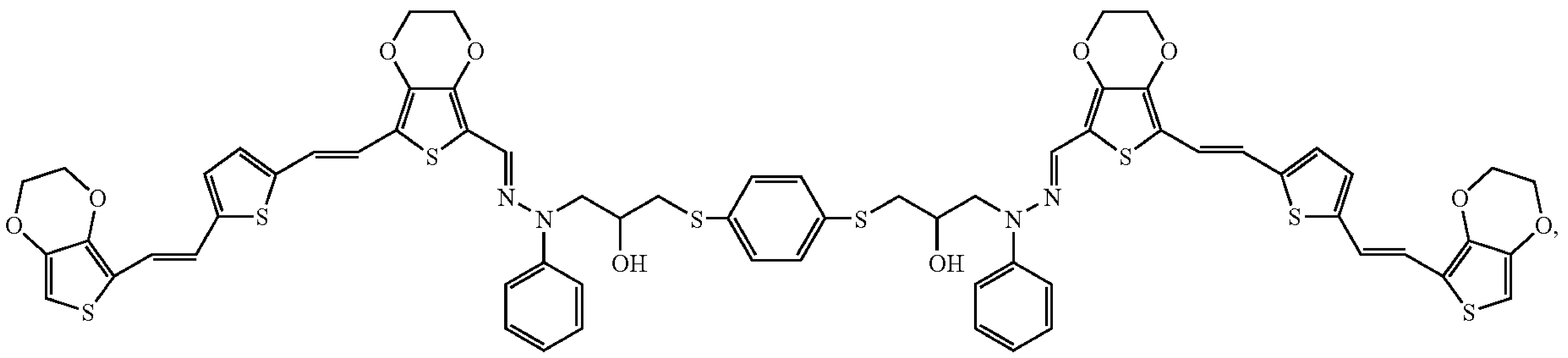


(3)

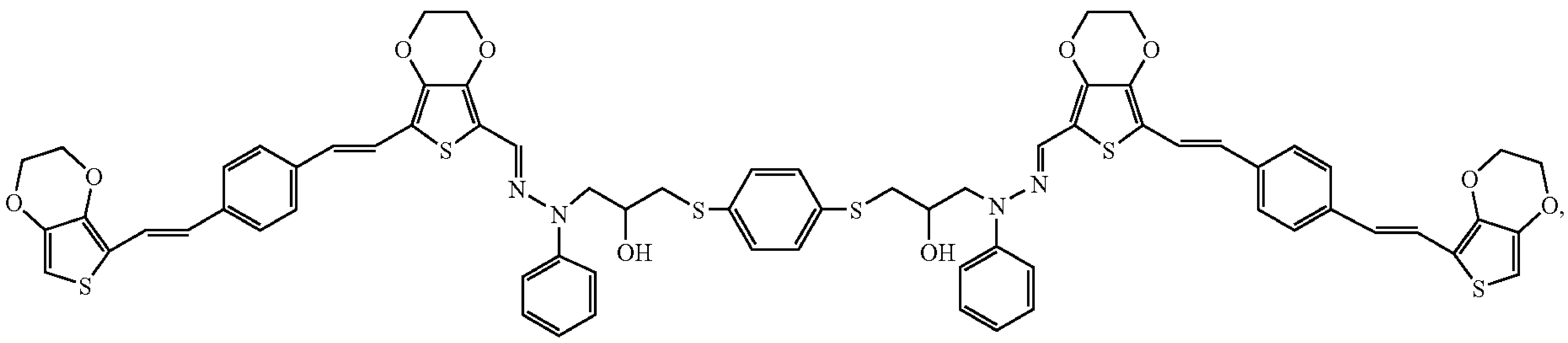


-continued

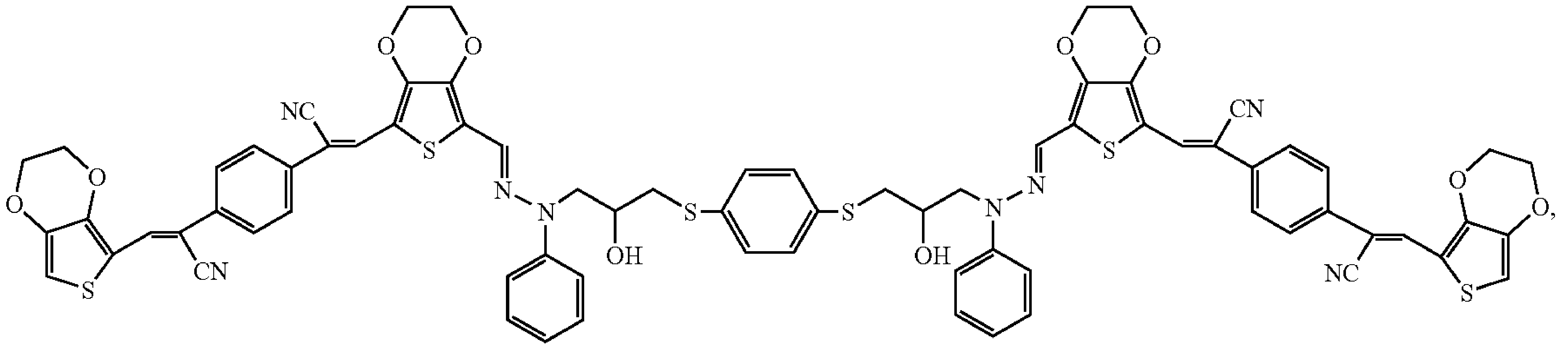
(4)



(5)

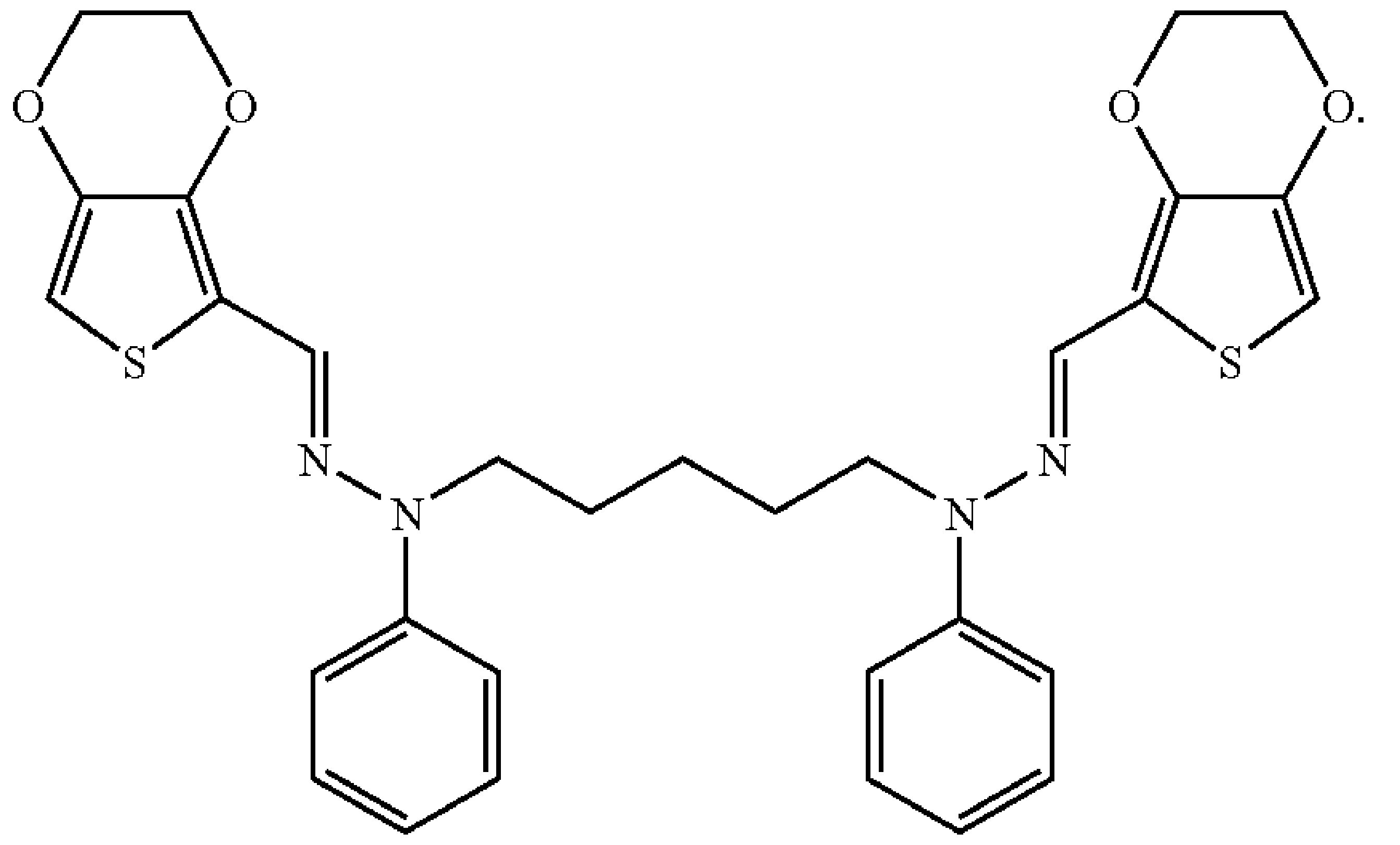


(6)



and

(7)

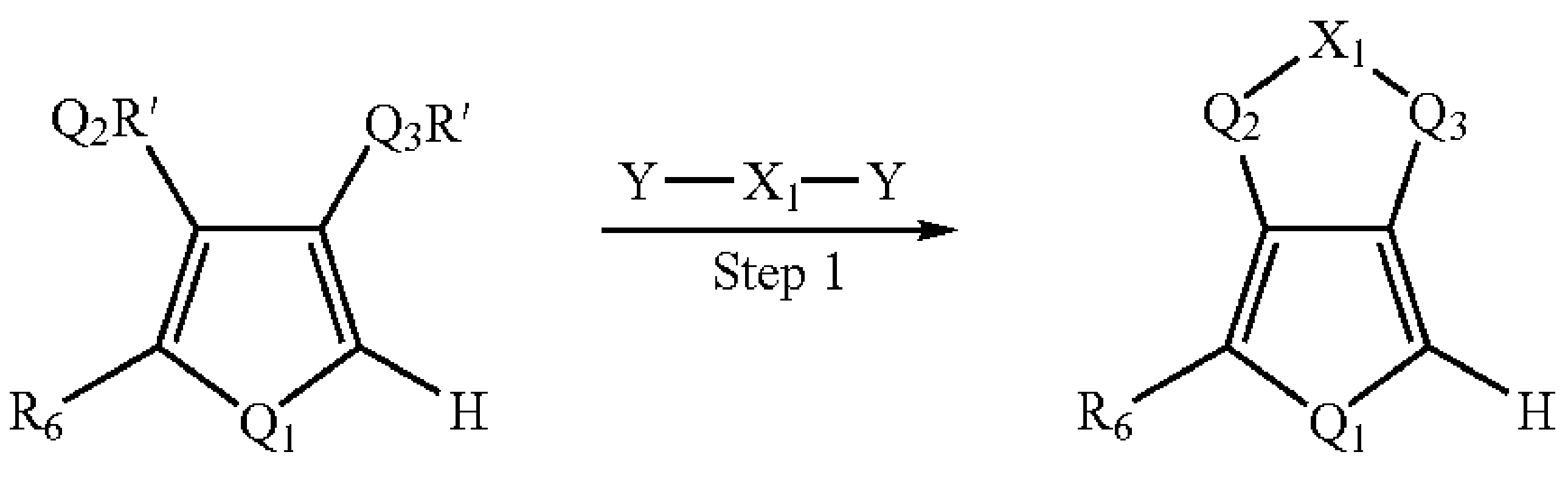


Synthesis Of Charge Transport Materials

The charge transport materials of this invention may be prepared by one of the following multi-step synthetic procedures, although other suitable procedures can be used by a person of ordinary skill in the art based on the disclosure herein.

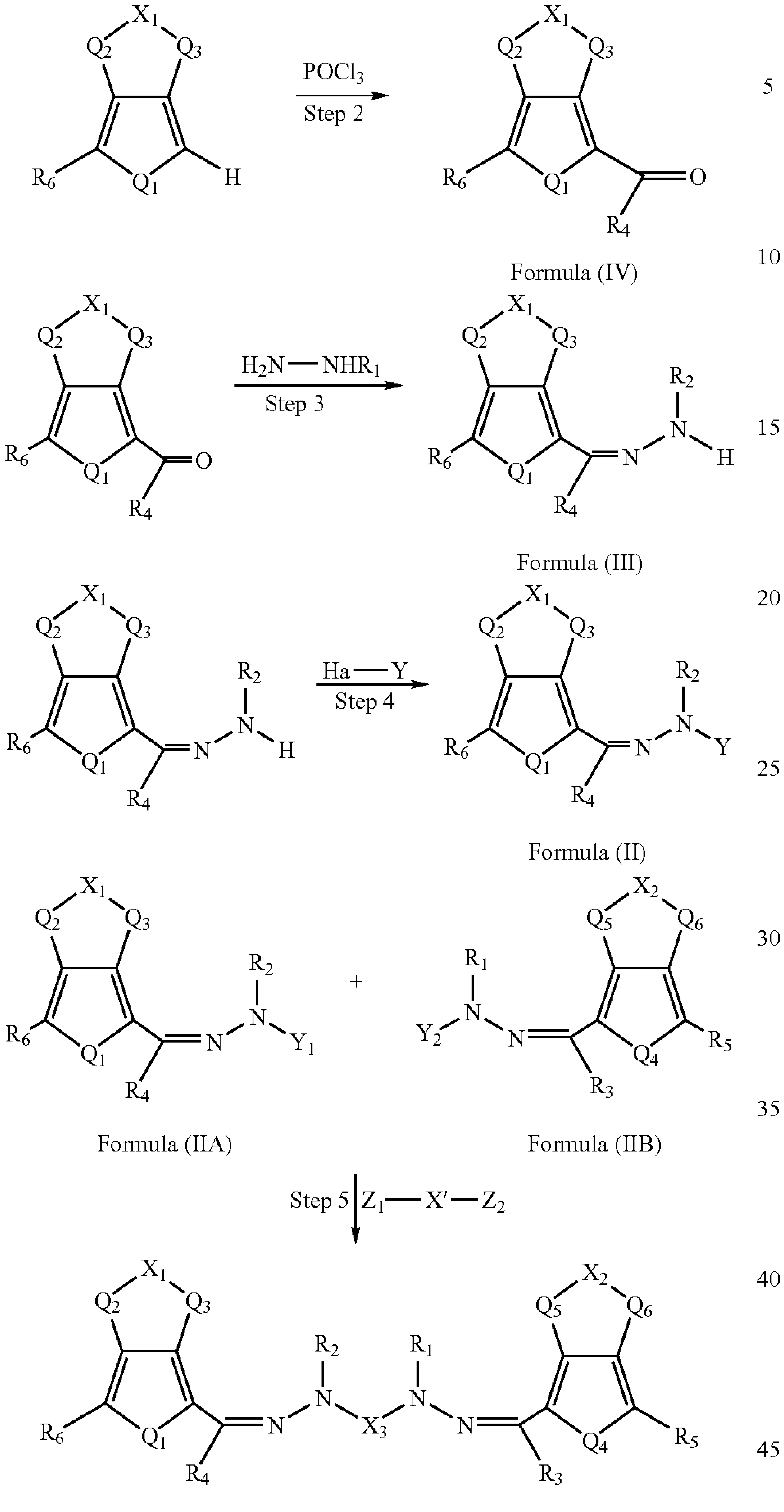
General Synthetic Procedures for Charge Transport Materials of Formula (I)

Procedure A



Formula (V)

-continued



Preparation of Formula (V). The bicyclic heterocycle of Formula (V) may be prepared by the reaction of a 5-membered heterocycle having 2 functional groups at the 3 and 4 positions with a dihalide having the formula $Y—X_1—Y$ where Y is F, Cl, Br, or I and the functional groups are selected independently from a group consisting of a hydroxyl group, a thiol group, amino groups, and a carboxyl group. Non-limiting examples of suitable dihalide include methylene dibromide, ethylene dibromide, 1,3-propylene dibromide, methylene dichloride, ethylene dichloride, 1,3-propylene dichloride, methylene diiodide, ethylene diiodide, and 1,3-propylene diiodide. Alternatively, the bicyclic heterocycle of Formula (V) may be prepared by the reaction of a 5-membered heterocycle having 2 alkoxy groups, such as a methoxy group, at the 3 and 4 positions with a difunctional compound having the formula $Y—X_1—Y$ where the Y groups are selected independently from a group consisting of a hydroxyl group, a thiol group, amino groups, and a carboxyl group. The difunctional compound may be a diol, a dithiol, a diamine, a dicarboxylic acid, a hydroxylamine, an amino acid, a hydroxyl acid, a thiol acid, a hydroxythiol, or a thioamine. Non-limiting examples of suitable dithiol are 3,6-dioxa-1,8-octanedithiol, erythro-1,4-dimercapto-2,3-butanediol, (±)-threo-1,4-dimercapto-2,3-butanediol, 4,4'-thiobisbenzenethiol, 1,4-benzenedithiol, 1,3-benzenedithiol, sulfonyl-bis(benzenethiol), 2,5-dimecapto-1,3,4-thiadiazole, 1,2-ethanedithiol, 1,3-propanedithiol, 1,4-butanedithiol, 2,3-butanedithiol, 1,5-pentanedithiol, and 1,6-hexanedithiol. Non-limiting examples of suitable diols are 2,2'-bi-7-naphtol, 1,4-dihydroxybenzene, 1,3-dihydroxybenzene, 10,10-bis(4-hydroxyphenyl)anthrone, 4,4'-sulfonyldiphenol, bisphenol, 4,4'-(9-fluorenylidene)diphenol, 1,10-decanediol, 1,5-pentanediol, diethylene glycol, 4,4'-(9-fluorenylidene)-bis(2-phenoxyethanol), bis(2-hydroxyethyl) terephthalate, bis[4-(2-hydroxyethoxy)phenyl]sulfone, hydroquinone-bis(2-hydroxyethyl)ether, and bis(2-hydroxyethyl)piperazine. Non-limiting examples of suitable diamine are diaminoarenes, and diaminoalkanes. Non-limiting examples of suitable dicarboxylic acid are phthalic acid, terephthalic acid, adipic acid, and 4,4'-biphenyldicarboxylic acid. Non-limiting examples of suitable hydroxylamine are p-aminophenol and fluoresceinamine. Non-limiting examples of suitable amino acid are 4-aminobutyric acid, phenylalanine, and 4-aminobenzoic acid. Non-limiting examples of suitable hydroxyl acid are salicylic acid, 4-hydroxybutyric acid, and 4-hydroxybenzoic acid. Non-limiting examples of suitable hydroxythiol are monothiohydroquinone and 4-mercapto-1-butanol. Non-limiting example of suitable thioamine is p-aminobenzenethiol. Non-limiting example of suitable thiol acid are 4-mercaptobenzoic acid and 4-mercaptobutyric acid. Almost all of the above difunctional compounds are available commercially from Aldrich and other chemical suppliers.

In some embodiments of interest, the bicyclic heterocycle of Formula (V) includes 3,4-alkylenedioxy ring compounds, such as 3,4-alkylenedioxythiophenes, 3,4-alkylenedioxyfurans, and 3,4-alkylenedioxypyrroles where Q_2 and Q_3 are each O. Such compounds are either known or may be prepared by reacting the corresponding 3,4-dihydroxythiophenes, 3,4-dihydroxyfurans, and 3,4-dihydroxypyrroles, where R' is H, with the appropriate alkylene dihalides, where Y is a halogen, such as F, Cl, Br, and I. Alternatively, 3,4-alkylenedioxythiophenes, 3,4-alkylenedioxyfurans, and 3,4-alkylenedioxypyrroles may be prepared by refluxing the corresponding 3,4-dimethoxythiophenes, 3,4-dimethoxyfurans, and 3,4-dimethoxypyrroles, where R' is a methyl group, with the appropriate alkylene diols, where Y is a hydroxyl group, in the presence of a catalytic amount of an acid, such as p-toluene sulfonic acid.

In other embodiments of interest, the bicyclic heterocycle of Formula (V) includes 3,4-alkylenedithia ring compounds, such as 3,4-alkylenedithiathiophenes, 3,4-alkylenedithiafurans, and 3,4-alkylenedithiapyrroles where Q_2 and Q_3 are each S. Such compounds may be prepared by reacting the corresponding 3,4-dithiothiophenes, 3,4-dithiofurans, and 3,4-dithiopyrroles, where R' is H, with the appropriate alkylene dihalides, where Y is a halogen, such as F, Cl, Br, and I. Alternatively, 3,4-alkylenedithiathiophenes, 3,4-alkylenedithiafurans, and 3,4-alkylenedithiapyrroles, may be prepared by refluxing the corresponding 3,4-dimethylsulfanylthiophenes, 3,4-dimethylsulfanylfurans, and 3,4-dimethylsulfanylpyrroles, where R' is a methyl group, with the appropriate alkylene diols, where Y is a hydroxyl group, in the presence of a catalytic amount of an acid, such as p-toluene sulfonic acid.

In further embodiments of interest, the bicyclic heterocycle of Formula (V) includes 3,4-alkylenediimine ring compounds, such as 3,4-alkylenediiminethiophenes, 3,4-alkylenediiminefurans, and 3,4-alkylenediiminepyrroles where Q_2 and Q_3 are each a NR group. Such compounds may be prepared by reacting the corresponding 3,4-diaminothiophenes, 3,4-diaminofurans, and 3,4-diaminopyrroles, where R' is H, with the appropriate alkylene dihalides, where Y is a halogen, such as F, Cl, Br, and I. Alternatively, alkylenediiminethiophenes, 3,4-alkylenediiminefurans, and 3,4-alkylenediiminepyrroles may be prepared by refluxing the corresponding 3,4-di(N-methylamino)thiophenes, 3,4-di(N-methylamino)furans, and 3,4-di(N-methylamino)pyrroles, where R' is a methyl group, with the appropriate alkylene diols, where Y is a hydroxyl group, in the presence of a catalytic amount of an acid, such as p-toluene sulfonic acid.

The preparations of 3,4-alkylenedioxythiophenes, 3,4-alkylenedioxyfurans, 3,4-alkylenedioxypyrroles, and 3,4-alkylenedithiothiophenes are described in Groenendaal et el., "Poly(3,4-ethylenedioxythiophene) and Its Derivatives: Past, Present, and Future," *Adv. Mater.,* 12, No. 7, pp. 481–494 (2000); Kros et al., "Poly(3,4-ethylenedioxythiophene)-Based Copolymers for Biosensor Applications," *Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 40, pp. 738–747 (2002); Zong et el., "3,4-Alkylenedioxy Ring Formation Via Double Mitsunobu Reactions: An Efficient Route for the Synthesis of 3,4-Ethylenedioxythiophene (Edot) and 3,4-Propylenedioxythiophene (Prodot) Derivatives as Monomers for Electron-Rich Conducting Polymers," *J. R. Chem. Commun*, pp. 2498–2499 (2002); U.S. Pat. No. 4,910,645; *Tetrahedron*, Vol. 23, pp. 2437–2441 (1967); *J. Am. Chem. Soc.,* 67, pp. 2217–2218 (1945); Pozo-Gonzalo et el., "Synthesis and electropolymerisation of 3',4'-bis(alkylsulfanyl)terthiophenes and the significance of the fused dithiin ring in 2,5-dithienyl-3,4-ethylenedithiothiophene (DT-EDTT)," *J. Mater. Chem.,* 12, pp. 500–510 (2002); and Kim et el., "New Conducting Polymers Based on Poly(3,4-ethylenedioxypyrrole): Synthesis, Characterization, and Properties," *Chemistry Letters*, Vol. 33, No. 1, pp. 46–47 (2004), all of which are incorporated herein by references.

Preparation of Formula (IV). The C-acylation of the bicyclic heterocycles of Formula (V) to form the acylated compounds of Formula (IV) may be done under Vilsmeier-Haack condition with a mixture of phosphorus oxychloride ($POCl_3$) and an N,N-dialkylamide, such as N,N-dimethylformamide, N,N-dimethylacetamide, and N,N-dimethylbenzamide. The C-acylations of thiophenes, furans, and pyrroles under Vilsmeier-Haack condition are described in Alan Katritzky, "Handbook of heterocyclic chemistry," Pergamon Press, New York, p. 254–255 (1985), which is incorporated herein by reference. Furthermore, the Vilsmeier-Haack acylation and related reactions are described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 380–393, which is incorporated herein by reference. Alternatively, the bicyclic heterocycles of Formula (V) may be acylated by a mixture of a strong base, such as butyl lithium, and an N,N-dialkylamide, or by a mixture of Lewis acid, such as stannic chloride, and an acid anhydride, such as acetic anhydride at an elevated temperature.

Specifically, the acylations of 3,4-ethylenedioxythiophene are described in Mohanakrishnan et al., "Functionalization of 3,4-ethylenedioxythiophene," Tetrahedron, 55, pp. 11745–11754 (1999), and by the procedure described in Sotzing et al., "Low Band Gap Cyanovinylene Polymers Based on Ethylenedioxythiophene," Macromolecules, 31, pp. 3750–3752 (1998), both of which are incorporated herein by reference.

Preparation of Formula (III). The (N-substituted)hydrazone of Formula (III) may be prepared by reacting the acylated compounds of Formula (IV) with the corresponding (N-substituted)hydrazines where R_1 comprises an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group. The reaction may be catalyzed by an appropriate amount of concentrated acid, such as sulfuric acid and hydrochloric acid.

Preparation of Formula (II). The (N,N-disubstituted)hydrazone of Formula (II) may be prepared by reacting the (N-substituted)hydrazone of Formula (III) with an organic halide having the formula Ha-Y where Ha is F, Cl, Br, or I; and Y (such as Y_1 and Y_2) may comprise a functional group selected from the group consisting of isocyanate, carbonyl, halides, hydroxyl, thiol, amino groups, carboxyl, and reactive ring groups, such as cyclic ethers (e.g., epoxides and oxetane), cyclic amines (e.g., aziridine), cyclic sulfides (e.g., thiirane), cyclic amides (e.g., 2-azetidinone, 2-pyrrolidone, 2-piperidone, caprolactam, enantholactam, and capryllactam), N-carboxy-α-amino acid anhydrides, lactones, and cyclosiloxanes. The chemistry of the above heterocyclic reactive ring group is described in George Odian, "Principle of Polymerization," second edition, Chapter 7, p. 508–552 (1981), incorporated herein by reference.

The Y group of the (N,N-disubstituted)hydrazone of Formula (II) may be an epoxy group. To prepare such an epoxy compound, Ha-Y should be an organic halide comprising an epoxy group. Non-limiting examples of suitable organic halide comprising an epoxy group as the reactive ring group are epihalohydrins, such as epichlorohydrin. The organic halide comprising an epoxy group can also be prepared by the epoxidation reaction of the corresponding alkene having a halide group. Such epoxidation reaction is described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 494–498, incorporated herein by reference. The alkene having a halide group can be prepared by the Wittig reaction between a suitable aldehyde or keto compound and a suitable Wittig reagent. The Wittig and related reactions are described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 69–77, which is incorporated herein by reference.

The Y group of the (N,N-disubstituted)hydrazone of Formula (II) may be a thiiranyl group. An epoxy compound, such as those described above, can be converted into the corresponding thiiranyl compound by refluxing the epoxy compound and ammonium thiocyanate in tetrahydrofuran. Alternatively, the corresponding thiiranyl compound may be obtained by passing a solution of the above-described epoxy compound through 3-(thiocyano)propyl-functionalized silica gel (commercially available form Aldrich, Milwaukee, Wis.). Alternatively, a thiiranyl compound may be obtained by the thia-Payne rearrangement of a corresponding epoxy compound. The thia-Payne rearrangement is described in Rayner, C. M. Synlett 1997, 11; Liu, Q. Y.; Marchington, A. P.; Rayner, C. M. Tetrahedron 1997, 53, 15729; Ibuka, T. Chem. Soc. Rev. 1998, 27, 145; and Rayner, C. M. Contemporary Organic Synthesis 1996, 3, 499. All the above four articles are incorporated herein by reference.

The Y group of the (N,N-disubstituted)hydrazone of Formula (II) may be an aziridinyl group. An aziridine compound may be obtained by the aza-Payne rearrangement of a corresponding epoxy compound, such as one of those epoxy compounds described above. The thia-Payne rearrangement is described in Rayner, C. M. Synlett 1997, 11; Liu, Q. Y.; Marchington, A. P.; Rayner, C. M. Tetrahedron 1997, 53, 15729; and Ibuka, T. Chem. Soc. Rev. 1998, 27, 145. All the above three articles are incorporated herein by reference. Alternatively, an aziridine compound may be prepared by the addition reaction between a suitable nitrene compound and a suitable alkene. Such addition reaction is described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 446–448, incorporated herein by reference.

The Y group of the (N,N-disubstituted)hydrazone of Formula (II) may be an oxetanyl group. An oxetane compound may be prepared by the Paterno-Buchi reaction between a suitable carbonyl compound and a suitable alkene. The Paterno-Buchi reaction is described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 335–336, incorporated herein by reference.

The Y group of the (N,N-disubstituted)hydrazone of Formula (II) may be a 5 or 7-membered ring comprising a —COO— group or a —CONR— group, such as butyrolactone, N-methylbutyrolactam, N-methylcaprolactam, and caprolactone.

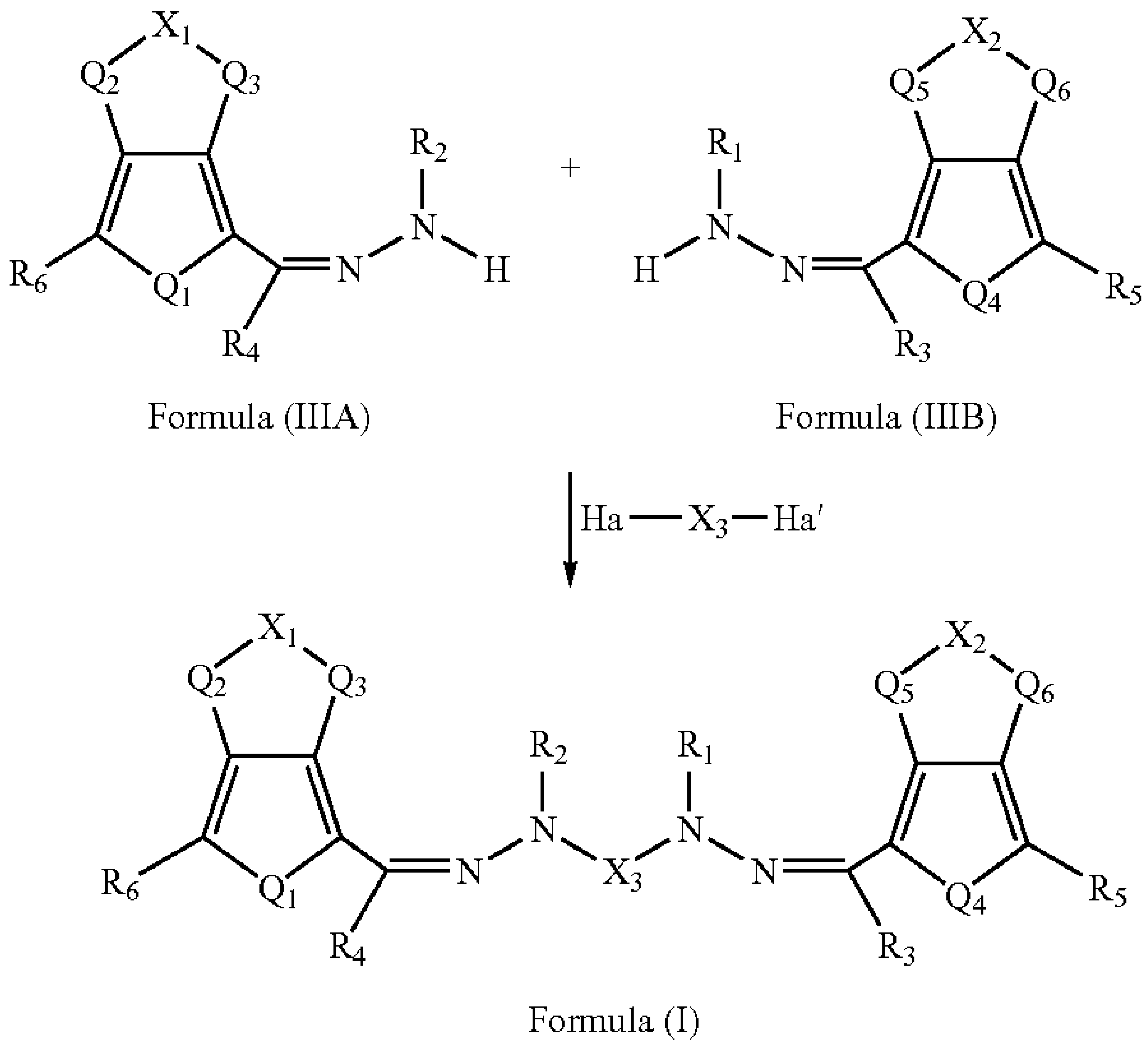
Preparation of Formula (I). The charge transport material of Formula (I) may be prepared by reacting at least one (N,N-disubstituted)hydrazone of Formula (II) with a bridging compound, Z_1-X'-Z_2 where Z_1 and Z_2 are, each independently, a functional group selected from the group consisting of isocyanate, carbonyl, halides, hydroxyl, thiol, amino groups, carboxyl, and reactive ring groups. In some embodiments, the bridging compound is selected from the group consisting of a diol, a dithiol, a diamine, a dicarboxylic acid, a hydroxylamine, an amino acid, a hydroxyl acid, a thiol acid, a hydroxythiol, and a thioamine.

Z_1 and Z_2 are selected in such a way that they can react with the Y group (such as Y_1 and Y_2). In some embodiments of interest, when the Y group is a hydroxyl or an amino group, Z_1 and Z_2 are, each independently, selected from the group consisting of isocyanates, halides, and carboxyl. In other embodiments, when the Y group is an amino group, Z_1 and Z_2 are, each independently, selected from the group consisting of carboxyl, carbonyl, and isocyanates. In further embodiments, when the Y group is hydroxyl, thiol, an amino group, or carboxyl, Z_1 and Z_2 are, each independently, selected from the group consisting of reactive ring groups. In additional embodiments, when the Y group is a reactive ring group, Z_1 and Z_2 are, each independently, selected from the group consisting of hydroxyl, thiol, amino groups, and carboxyl. The X_3 group is formed by the reactions of Y_1, Z_1-X'-Z_2, and Y_2.

When a symmetrical charge transport material of Formula (I) is desired, the (N,N-disubstituted)hydrazone of Formula (IIA) should be the same as the (N,N-disubstituted)hydrazone of Formula (IIB) and the bridging compound, Z_1-X'-Z_2, should be symmetrical. When an unsymmetrical charge transport material of Formula (I) is desired, the (N,N-disubstituted)hydrazone of Formula (IIA) should be different from the (N,N-disubstituted)hydrazone of Formula (IIB) and the bridging compound, Z_1-X'-Z_2, should be unsymmetrical. To prepare an unsymmetrical charge transport material of Formula (I), a bridging compound may react with two different (N,N-disubstituted)hydrazone of Formula (II) in two sequential reactions. In the first reaction, an excess of the bridging compound may be used to maximize the desirable product and to minimize the undesirable symmetrical side product. In the second reaction, the product obtained in the first reaction may react with a second (N,N-disubstituted)hydrazone of Formula (II) to form the desirable unsymmetrical charge transport material of Formula (I).

The desired product, either symmetrical or unsymmetrical, may be isolated and purified by the conventional purification techniques such as column chromatography and recrystallization.

Procedure B



Alternatively, the charge transport material of Formula (I) may be prepared by reacting at least an (N-substituted) hydrazone of Formula (III) with a dihalide (Ha-X_3-Ha' where Ha and Ha' are, each independently, F, Cl, Br, or I), such as dibromides, diiodides, dichlorides, and difluorides, in the presence of a base, such as sodium hydroxide, in a polar solvent, such as dimethyl sulfoxide, at an elevated temperature. Non-limiting examples of suitable dihalide include 1,4-dibromobutane, 1,5-dibromopentane, 1,8-dibromooctane, and 1,10-dibromodecane.

When a symmetrical charge transport material of Formula (I) is desired, the (N-substituted)hydrazone of Formula (IIIA) should be the same as the (N-substituted)hydrazone of Formula (IIIB) and the dihalide, Ha-X_3-Ha', should be symmetrical. When an unsymmetrical charge transport material of Formula (I) is desired, the (N-substituted)hydrazone of Formula (IIIA) should be different from the (N-substituted)hydrazone of Formula (IIIB) and the dihalide, Ha-X_3-Ha', should be unsymmetrical. To prepare an unsymmetrical charge transport material of Formula (I), a bridging compound may react with two different (N-substituted) hydrazone of Formula (III) in two sequential reactions. In the first reaction, an excess of the bridging compound may be used to maximize the desirable product and to minimize the undesirable symmetrical side product. In the second reaction, the product obtained in the first reaction may react with a second (N-substituted)hydrazone (III) to form the desirable unsymmetrical charge transport material of Formula (I).

The desired product, either symmetrical or unsymmetrical, may be isolated and purified by the conventional purification techniques such as column chromatography and recrystallization.

The invention will now be described further by way of the following examples.

EXAMPLES

Example 1

Synthesis and Characterization Charge Transport Materials

This example describes the synthesis and characterization of Compounds (1)–(7) in which the numbers refer to formula numbers above. The characterization involves chemical characterization of the compounds. The electrostatic characterization, such as mobility and ionization potential, of the materials formed with the compounds is presented in a subsequent example.

Compound (1)

3,4-Ethylenedioxythiophene-2-carbaldehyde. 3,4-Ethylenedioxythiophene-2-carbaldehyde may be prepared by the procedure described in Mohanakrishnan et al., "Functionalization of 3,4-ethylenedioxythiophene," Tetrahedron, 55, pp. 11745–11754 (1999), which is incorporated herein by reference. Alternatively, 3,4-ethylenedioxythiophene-2-carbaldehyde may be prepared by the procedure described in Sotzing et al., "Low Band Gap Cyanovinylene Polymers Based on Ethylenedioxythiophene," Macromolecules, 31, pp. 3750–3752 (1998), which is incorporated herein by reference.

3,4-Ethylenedioxythiophene-2-carbaldehyde N-Phenylhydrazone. In a 250 ml round bottomed flask, 3,4-ethylenedioxythiophene-2-carbaldehyde (5 g, 0.0294 mol) was dissolved in 120 ml of methanol by heat. A solution of N-phenylhydrazine (4.76 g, 0.0441 mol) in methanol was added to the cooled reaction mixture. After the reaction mixture was heated at 65° C. for 2.5 hours, the reaction mixture was concentrated and then placed in a freezer to form yellowish crystals of 3,4-ethylenedioxythiophene-2-carbaldehyde N-phenylhydrazone. The yellowish crystals were filtered off, washed with a large amount of cold methanol, and dried. The yield of 3,4-ethylenedioxythiophene-2-carbaldehyde N-phenylhydrazone was 4.73 g (62%). The melting point of the product was found to be 136–137° C. The ^{1}H-NMR spectrum (100 MHz) of the product in $CDCl_3$ was characterized by the following chemical shifts (δ, ppm): 7.81 (s, 1H, CH═N), 7.4–6.95 (m, 4H, Ar), 6.82 (t, 1H, J=5.3 Hz, 4-H_{Ph}), 6.26 (s, 1H, CH═S), and 4.4–4.1 (m, 4H, OCH_2CH_2). The infrared absorption spectrum of the product was characterized by the following absorption peaks (KBr window, cm^{-1}): 3124, 3058 (arene C—H); 2976, 2922, 2869 (CH); 1595, 1500, 1442 (C═C in Ar, C═N); 1069, 935, 907 (C—O); 760 (Ar). The mass spectrum of the product was characterized by the following m/z peak: 261 (100%, M+1).

3,4-Ethylenedioxythiophene-2-carbaldehyde N-(2,3-Epoxypropyl)-N-Phenylhydrazone. 3,4-Ethylenedioxythiophene-2-carbaldehyde N-phenylhydrazone (4.6 g, 0.0097 mol) was dissolved in 24.5 g of epichlorohydrin in a 100 ml round bottomed flask. Potassium hydroxide (3.8 g, 0.068 mol) was added to the reaction mixture in five additions. Additionally 0.25 g of sodium sulfate was added before every addition of KOH to the flask. After the reaction mixture was stirred for 15 hours at room temperature, it was filtered and then epichlorohydrin was removed by vacuum distillation. The crude product was purified by a silica gel column with an eluant mixture of ethyl acetate and n-hexane in a volume ratio of 1:2. The product, 3,4-ethylenedioxythiophene-2-carbaldehyde N-(2,3-epoxypropyl)-N-phenylhydrazone, was recrystallized from diethyl ether. The yield of the product was 58% (1.76 g). The melting point of the product was found to be 107–108° C. The ^{1}H-NMR spectrum (100 MHz) of the product in $CDCl_3$ was characterized by the following chemical shifts (δ, ppm): 7.79 (s, 1H, CH═N), 7.5–7.25 (m, 4H, Ar), 7.05–6.8 (m, 1H, 4-H_{Ph}), 6.23 (s, 1H, CH═S), 4.43–4.27 (dd, 1H, one of NCH_2 protons, (H_A), J_{AX}=2.9 Hz, J_{AB}=9.7 Hz), 4.1–3.78 (dd, 1H, another NCH_2 proton, (H_B), J_{BX}=4 Hz), 3.24 (m, 1H, CH), 2.87 (t, one of OCH_2 protons, (H_B), J_{BX}=4.2 Hz), and 2.7–2.55 (dd, 1H, CH_2O another proton, (H_A), J_{AX}=2.7 Hz). The infrared absorption spectrum of the product was characterized by the following absorption peaks (KBr window, cm^{-1}): 3124, 3058 (arene C—H); 2976, 2922, 2869 (CH); 1595, 1500, 1442 (C═C in Ar, C═N); 1069, 935, 907 (C—O); 760 (Ar). The mass spectrum of the product was characterized by the following m/z peak: 317 (100%, M+1).

Three drops of triethylamine were slowly added to the solution of 0.7 g (2.2 mmol) of 3,4-ethylenedioxythiophene-2-carbaldehyde N-(2,3-epoxypropyl)-N-phenylhydrazone and 0.26 g (1.0 mmol) of 4,4'-thiobisbenzenethiol in 10 ml of 2-butanone, while the temperature of the reaction mixture was maintained below 30° C. The reaction mixture was kept overnight at room temperature. After the evaporation of the solvent, the residue was purified by a silica gel column using an eluant mixture of dichloromethane and ethyl acetate. The yield of the yellow amorphous product, Compound (1), was 0.64 g (73%). The ^{1}H-NMR spectrum (100 MHz) of the product in $CDCl_3$ was characterized by the following chemical shifts (δ, ppm): 7.99 (s, 2H, CH═N), 7.6–7.1 (m, 16H, Ar), 6.95–6.7 (m, 2H, Ar), 6.48 (s, 2H, CH═S); 5.6 (s, 2H, OH); 4.24 (s, 8H, OCH_2CH_2O); 4.15–3.8 (m, 6H, C$\underline{H}$OH, NC$\underline{H}_2$CH); and 3.05–3.27 (m, 4H, CH_2S). The infrared absorption spectrum of Compound (1) was characterized by the following absorptions (KBr window, cm^{-1}): 3426 (OH), 3105 (Ar C—H), 2977, 2921, 2870, (Alk C—H), 1596, 1515, 1439 (Ar C═C), and 1146 (C—N).

Compound (2)

Compound (2) was prepared similarly by the procedure for Compound (1) above except that 4,4'-thiobisbenzenethiol was replaced by 1,3-benzenedithiol (from Aldrich, Milwaukee, Wis.). Three drops of triethylamine were slowly added to a solution of 0.81 g (2.56 mmol) of 3,4-ethylenedioxythiophene-2-carbaldehyde N-(2,3-epoxypropyl)-N-phenylhydrazone and 0.158 g (1.13 mmol) of 1,3-benzenedithiol in 15 ml of 2-butanone, while the temperature of the reaction mixture was maintained below 30° C. The reaction mixture then was kept overnight at the room temperature. After the evaporation of the solvent, the residue was subjected to chromatography (silica gel, Aldrich) using a mixture of dichloromethane and ethyl acetate for the final eluting of the product. The ^{1}H-NMR spectrum (100 MHz) of the product in d_6-DMSO was characterized by the following chemical shifts (δ, ppm): 7.95 (s, 2H, CH═N), 7.6–6.7 (m, 14H, Ar), 6.48 (s, 2H, CH═S); 5.5 (s, 2H, OH); 4.21 (s, 8H, OCH_2CH_2O); 4.15–3.8 (m, 6H, CHOH, NCH_2CH); 3.05–3.27 (m, 4H, CH_2S).

Compound (3)

2,5-Bis[(3,4-ethylenedioxy)thien-2-yl]-1,3,4-oxadiazole may be prepared according to the procedure described in Pepitone et al, "Synthesis and Characterization of Photoluminescent 3,4-Ethylenedioxythiophene Derivatives," Chem. Mater. 15, pp. 557–563 (2003), which is incorporated herein by reference.

2-[(2-Formyl-3,4-ethylenedioxy)thien-5-yl]-5-[(3,4-ethylenedioxy)thien-2-yl]-1,3,4-oxadiazole may be prepared by the following procedure which is similar to the procedure described in Mohanakrishnan et al., “Functionalization of 3,4-ethylenedioxythiophene,” Tetrahedron, 55, pp. 11745–11754 (1999), incorporated herein by reference. A solution of 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-1,3,4-oxadiazole (4.94 g, 0.0141 mol) in dry tetrahydrofuran (30 ml) is cooled to −78° C. under nitrogen, treated with 6.2 ml of 2.5 M n-butyl lithium in hexane (available from Aldrich) and the temperature is raised to 0° C. After the mixture is stirred at 0° C. for 30 minutes, it is recooled to −78° C. and treated with dry N,N-dimethylformamide (2 ml, 0.026 mol). The mixture is then stirred at room temperature for 4 hours and poured into crushed ice containing hydrochloric acid. The product, 2-[(2-formyl-3,4-ethylenedioxy)thien-5-yl]-5-[(3,4-ethylenedioxy)thien-2-yl]-1,3,4-oxadiazole, is filtered, washed with water, and dried in a vacuum oven. The product may be further purified by conventional recrystallization or chromatography techniques. Alternatively, 2-[(2-Formyl-3,4-ethylenedioxy)thien-5-yl]-5-[(3,4-ethylenedioxy)thien-2-yl]-1,3,4-oxadiazole may be prepared by the Vilsmeier formylation of 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-1,3,4-oxadiazole with a mixture of N,N-dimethylformamide and phosphorous oxychloride.

Compound (3) may be prepared by the procedure for Compound (1) above except that 3,4-ethylenedioxythiophene-2-carbaldehyde is replaced by 2-[(2-formyl-3,4-ethylenedioxy)thien-5-yl]-5-[(3,4-ethylenedioxy)thien-2-yl]-1,3,4-oxadiazole and that 4,4'-thiobisbenzenethiol is replaced by 1,4-benzenedithiol.

Compound (4)

2,2'-(3,4-Ethylenedioxy)dithienyl-ω,ω'-2,5-divinylthiophene may be prepared according to the procedure described in Mohanakrishnan et al., “Functionalization of 3,4-ethylenedioxythiophene,” Tetrahedron, 55, pp. 11745–11754 (1999), which is incorporated herein by reference.

2-(3,4-Ethylenedioxythienyl)-2'-(5-formyl-3,4-ethylenedioxythienyl)-ω,ω'-2,5-divinylthiophene may be prepared by the following procedure which is similar to the procedure described in Mohanakrishnan et al., “Functionalization of 3,4-ethylenedioxythiophene,” Tetrahedron, 55, pp. 11745–11754 (1999), incorporated herein by reference. A solution of 2,2'-(3,4-ethylenedioxy)dithienyl-ω,ω'-2,5-divinylthiophene (5.41 g, 0.0141 mol) in dry tetrahydrofuran (30 ml) is cooled to −78° C. under nitrogen treated with 6.2 ml of 2.5 M n-butyl lithium in hexane (available from Aldrich) and the temperature is raised to 0° C. After the mixture is stirred at 0° C. for 30 minutes, it is recooled to −78° C. and treated with dry N,N-dimethylformamide (2 ml, 0.026 mol). The mixture is then stirred at room temperature for 4 hours and poured into crushed ice containing hydrochloric acid. The product, 2-(3,4-ethylenedioxythienyl)-2'-(5-formyl-3,4-ethylenedioxythienyl)-ω,ω'-2,5-divinylthiophene, is filtered, washed with water, and dried in a vacuum oven. The product may be further purified by conventional recrystallization or chromatography techniques. Alternatively, 2-(3,4-ethylenedioxythienyl)-2'-(5-formyl-3,4-ethylenedioxythienyl)-ω,ω'-2,5-divinylthiophene may be prepared by the Vilsmeier formylation of 2,2'-(3,4-ethylenedioxy)dithienyl-ω,ω'-2,5-divinylthiophene with a mixture of N,N-dimethylformamide and phosphorous oxychloride.

Compound (4) may be prepared by the procedure for Compound (1) above except that 3,4-ethylenedioxythiophene-2-carbaldehyde is replaced by 2-(3,4-ethylenedioxythienyl)-2'-(5-formyl-3,4-ethylenedioxythienyl)-ω,ω'-2,5-divinylthiophene and that 4,4'-thiobisbenzenethiol is replaced by 1,4-benzenedithiol.

Compound (5)

2,2'-(3,4-Ethylenedioxy)dithienyl-ω,ω'-1,4-divinyl benzene may be prepared according to the procedure described in Mohanakrishnan et al., “Functionalization of 3,4-ethylenedioxythiophene,” Tetrahedron, 55, pp. 11745–11754 (1999), which is incorporated herein by reference.

2-(3,4-Ethylenedioxythienyl)-2'-(5-formyl-3,4-ethylenedioxythienyl)-ω,ω'-1,4-divinyl benzene may be prepared by the following procedure which is similar to the procedure described in Mohanakrishnan et al., “Functionalization of 3,4-ethylenedioxythiophene,” Tetrahedron, 55, pp. 11745–11754 (1999), incorporated herein by reference. A solution of 2,2'-(3,4-ethylenedioxy)dithienyl-ω,ω'-1,4-divinyl benzene (5.78 g, 0.0141 mol) in dry tetrahydrofuran (30 ml) is cooled to −78° C. under nitrogen treated with 6.2 ml of 2.5 M n-butyl lithium in hexane (available from Aldrich) and the temperature is raised to 0° C. After the mixture is stirred at 0° C. for 30 minutes, it is recooled to −78° C. and treated with dry N,N-dimethylformamide (2 ml, 0.026 mol). The mixture is then stirred at room temperature for 4 hours and poured into crushed ice containing hydrochloric acid. The product, 2-(3,4-ethylenedioxythienyl)-2'-(5-formyl-3,4-ethylenedioxythienyl)-ω,ω'-1,4-divinyl benzene, is filtered, washed with water, and dried in a vacuum oven. The product may be further purified by conventional recrystallization or chromatography techniques. Alternatively, 2-(3,4-ethylenedioxythienyl)-2'-(5-formyl-3,4-ethylenedioxythienyl)-ω,ω'-1,4-divinyl benzene may be prepared by the Vilsmeier formylation of 2,2'-(3,4-ethylenedioxy)dithienyl-ω,ω'-2,5-divinyl benzene with a mixture of N,N-dimethylformamide and phosphorous oxychloride.

Compound (5) may be prepared by the procedure for Compound (1) above except that 3,4-ethylenedioxythiophene-2-carbaldehyde is replaced by 2-(3,4-ethylenedioxythienyl)-2'-(5-formyl-3,4-ethylenedioxythienyl)-ω,ω'-1,4-divinyl benzene and that 4,4'-thiobisbenzenethiol is replaced by 1,4-benzenedithiol.

Compound (6)

1,4-Bis[(1-cyano-2-{(3,4-ethylenedioxy)thien-2-yl}vinyl]benzene may be prepared according to the procedure described in Pepitone et al, “Synthesis and Characterization of Photoluminescent 3,4-Ethylenedioxythiophene Derivatives,” Chem. Mater. 15, pp. 557–563 (2003), which is incorporated herein by reference.

1-[(1-Cyano-2-{(3,4-ethylenedioxy)thien-2-yl}vinyl]-4-[(1-cyano-2-{(5-formyl-3,4-ethylenedioxy)thien-2-yl}vinyl]benzene may be prepared by the following procedure which is similar to the procedure described in Mohanakrishnan et al., “Functionalization of 3,4-ethylenedioxythiophene,” Tetrahedron, 55, pp. 11745–11754 (1999), incorporated herein by reference. A solution of 1,4-bis[(1-cyano-2-{(3,4-ethylenedioxy)thien-2-yl}vinyl]benzene (6.49 g, 0.0141 mol) in dry tetrahydrofuran (30 ml) is cooled to −78° C. under nitrogen treated with 6.2 ml of 2.5 M n-butyl lithium in hexane (available from Aldrich) and the temperature is raised to 0° C. After the mixture is stirred at 0° C. for 30 minutes, it is recooled to −78° C. and treated with dry N,N-dimethyl formamide (2 ml, 0.026 mol). The mixture is then stirred at room temperature for 4 hours and poured into crushed ice containing hydrochloric acid. The product is filtered, washed with water, and dried in a vacuum oven. The product may be further purified by conventional recrystallization or chromatography techniques. Alternatively, 1-[(1-cyano-2-{(3,4-ethylenedioxy)thien-2-yl}vinyl]-4-[(1-cyano-2-{(5-formyl-3,4-ethylenedioxy) thien-2-yl}vinyl]benzene may be prepared by the Vilsmeier formylation of 1,4-bis[(1-cyano-2-{(3,4-ethylenedioxy) thien-2-yl}vinyl] benzene with a mixture of N,N-dimethylformamide and phosphorous oxychloride.

Compound (6) may be prepared by the procedure for Compound (1) above except that 3,4-ethylenedioxythiophene-2-carbaldehyde is replaced by 1-[(1-cyano-2-{(3,4-ethylenedioxy)thien-2-yl}vinyl]-4-[(1-cyano-2-{(5-formyl-3,4-ethylenedioxy)thien-2-yl}vinyl]benzene and that 4,4'-thiobisbenzenethiol is replaced by 1,4-benzenedithiol.

Compound (7)

Compound (7) may be prepared by the following procedure. A mixture of 3,4-ethylenedioxythiophene-2-carbaldehyde N-phenylhydrazone (0.1 mole, prepared as an intermediate for Compound (1) above) and dimethyl sulfoxide (50 ml) is added to a 250 ml 3-neck round bottom flask equipped with thermometer and mechanical stirrer. After the solid is dissolved, 1,5-dibromopentane (0.05 mole, from Aldrich Chemical Company) and then an aqueous solution of 50% sodium hydroxide (20 g) are added. The reaction mixture is heated to 85° C. for 2 hours. After the mixture is cooled to room temperature, it is poured into 2 L of water. The product may be isolated and purified by conventional recrystallization and/or chromatography techniques.

Example 2

Charge Mobility Measurements

This example describes the measurement of charge mobility and ionization potential for charge transport materials, specifically Compound (1).

Sample 1

A mixture of 0.1 g of the Compound (1) and 0.1 g of polycarbonate Z (commercially obtained from Mitsubishi Engineering Plastics Corp, White Plain, N.Y.) was dissolved in 2 ml of tetrahydrofuran (THF). The solution was coated on a polyester film with a conductive aluminum layer by a dip roller. After the coating was dried for 1 hour at 80° C., a clear 10 μm thick layer was formed. The hole mobility of the sample was measured and the results are presented in Table 1.

Sample 2

Sample 2 was prepared and tested similarly to Sample 1, except Compound (1) was replaced with Compound (2).

Mobility Measurements

Each sample was corona charged positively up to a surface potential U and illuminated with 2 ns long nitrogen laser light pulse. The hole mobility μ was determined as described in Kalade et al., "Investigation of charge carrier transfer in electrophotographic layers of chalkogenide glasses," Proceeding IPCS 1994: The Physics and Chemistry of Imaging Systems, Rochester, N.Y., pp. 747–752, incorporated herein by reference. The hole mobility measurement was repeated with appropriate changes to the charging regime to charge the sample to different U values, which corresponded to different electric field strength inside the layer E. This dependence on electric field strength was approximated by the formula

$$\mu=\mu_0 e^{\alpha\sqrt{E}}.$$

Here E is electric field strength, μ_0 is the zero field mobility and α is Pool-Frenkel parameter. Table 1 lists the mobility characterizing parameters μ_0 and α values and the mobility value at the 6.4×10^5 V/cm field strength as determined by these measurements for the four samples.

TABLE 1

Example	μ_0 (cm^2/V·s)	μ (cm^2/V·s) at $6.4\cdot10^5$ V/cm	α $(cm/V)^{0.5}$	Ionization Potential (eV)
Compound (1)	/	/	/	5.6
Sample 1	5.6×10^{-10}	1.1×10^{-7}	0.0066	/
Compound (2)	/	/	/	5.54
Sample 2	2.0×10^{-11}	3.0×10^{-9}	0.0063	/

Example 3

Ionization Potential Measurements

This example describes the measurement of the ionization potential for the charge transport materials described in Example 1.

To perform the ionization potential measurements, a thin layer of a charge transport material about 0.5 μm thickness was coated from a solution of 2 mg of the charge transport material in 0.2 ml of tetrahydrofuran on a 20 cm^2 substrate surface. The substrate was an aluminized polyester film coated with a 0.4 μm thick methylcellulose sub-layer.

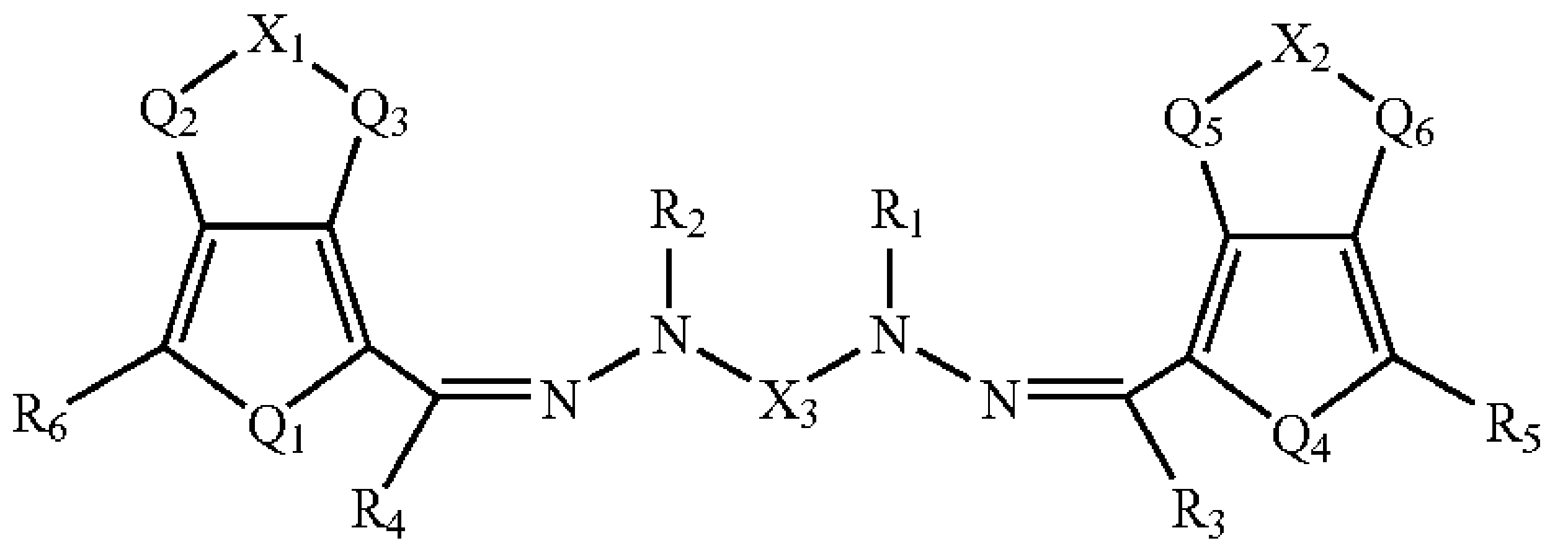
Ionization potential was measured as described in Grigalevicius et al., "3,6-Di(N-diphenylamino)-9-phenylcarbazole and its methyl-substituted derivative as novel hole-transporting amorphous molecular materials," Synthetic Metals 128 (2002), p. 127–131, incorporated herein by reference. In particular, each sample was illuminated with monochromatic light from the quartz monochromator with a deuterium lamp source. The power of the incident light beam was $2\text{–}5\cdot10^{-8}$ W. A negative voltage of −300 V was supplied to the sample substrate. A counter-electrode with the 4.5×15 mm^2 slit for illumination was placed at 8 mm distance from the sample surface. The counter-electrode was connected to the input of a BK2-16 type electrometer, working in the open input regime, for the photocurrent measurement. A $10^{-15}\text{–}10^{-12}$ amp photocurrent was flowing in the circuit under illumination. The photocurrent, I, was strongly dependent on the incident light photon energy hν. The $I^{0.5}=f(h\nu)$ dependence was plotted. Usually, the dependence of the square root of photocurrent on incident light quanta energy is well described by linear relationship near the threshold (see references "Ionization Potential of Organic Pigment Film by Atmospheric Photoelectron Emission Analysis," *Electrophotography,* 28, Nr. 4, p. 364 (1989) by E. Miyamoto, Y. Yamaguchi, and M. Yokoyama; and "Photoemission in Solids," Topics in Applied Physics, 26, 1–103 (1978) by M. Cordona and L. Ley, both of which are incorporated herein by reference). The linear part of this dependence was extrapolated to the hν axis, and the Ip value was determined as the photon energy at the interception point. The ionization potential measurement has an error of ±0.03 eV. The ionization potential values are given in Table 1 above.

As understood by those skilled in the art, additional substitution, variation among substituents, and alternative methods of synthesis and use may be practiced within the scope and intent of the present disclosure of the invention. The embodiments above are intended to be illustrative and not limiting. Additional embodiments are within the claims. Although the present invention has been described with reference to particular embodiments, workers skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.

What is claimed is:

1. An organophotoreceptor comprising an electrically conductive substrate and a photoconductive element on the electrically conductive substrate, the photoconductive element comprising:

(a) a charge transport material having the formula



where R_1, R_2, R_3, R_4, R_5, and R_6 comprise, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group;

X_1 and X_2 are, each independently, a —$(CH_2)_n$— group, where n is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, C=O, O=S=O, an NR_a group, or a CR_cR_d group, where R_a, R_c, and R_d, are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, or an alkoxy group;

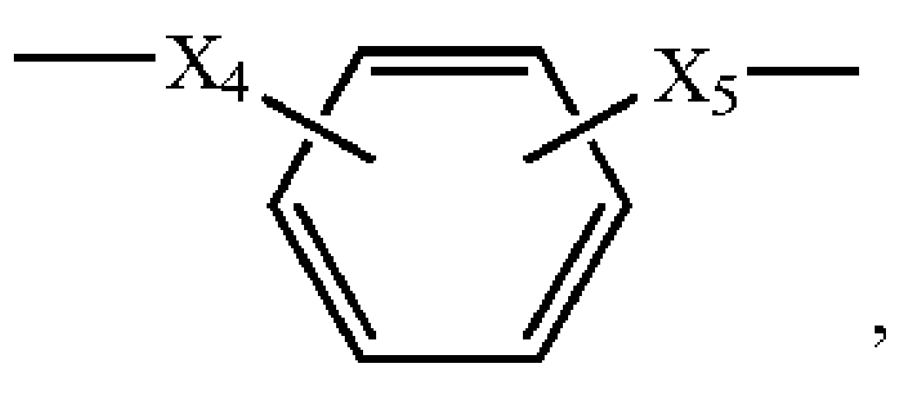
X_3 is linking group; and

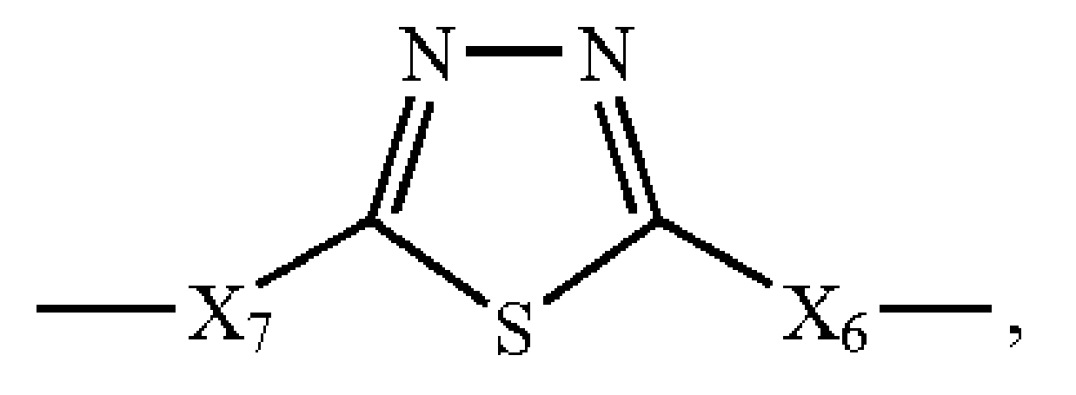
Q_1, Q_2, Q_3, Q_4, Q_5, and Q_6 are, each independently, O, S, NR, where R is, H, or an alkyl group; and

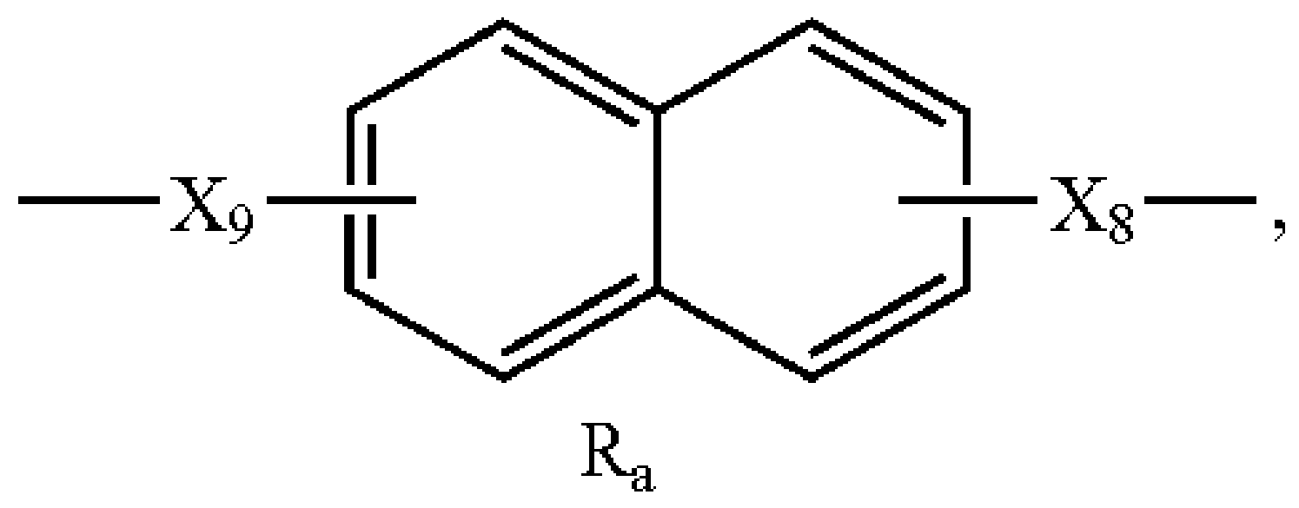
(b) a charge generating compound.

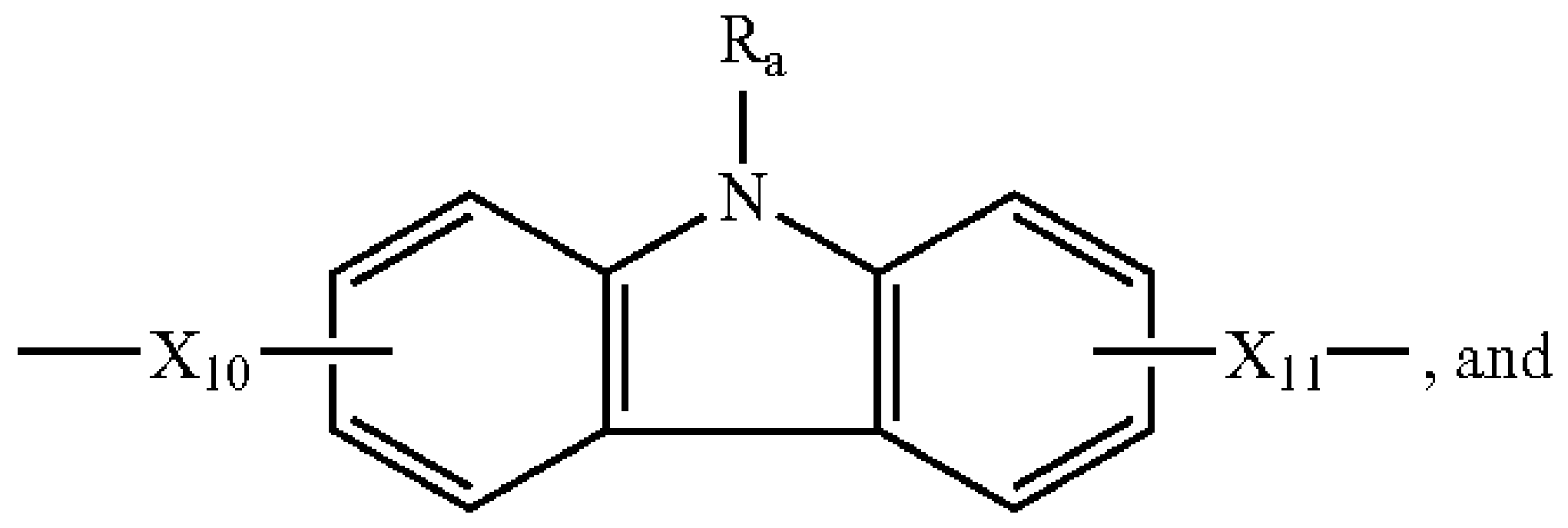
2. An organophotoreceptor according to claim **1** wherein X_3 comprises a —$(CH_2)_m$— group, where m is an integer between 1 and 50, inclusive, and one or more of the methylene groups is optionally replaced by O, S, C=O, O=S=O, an aromatic group, an NR_i group, or a CR_kR_l group, where R_i, R_k, and R_l, are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, or an alkoxy group.

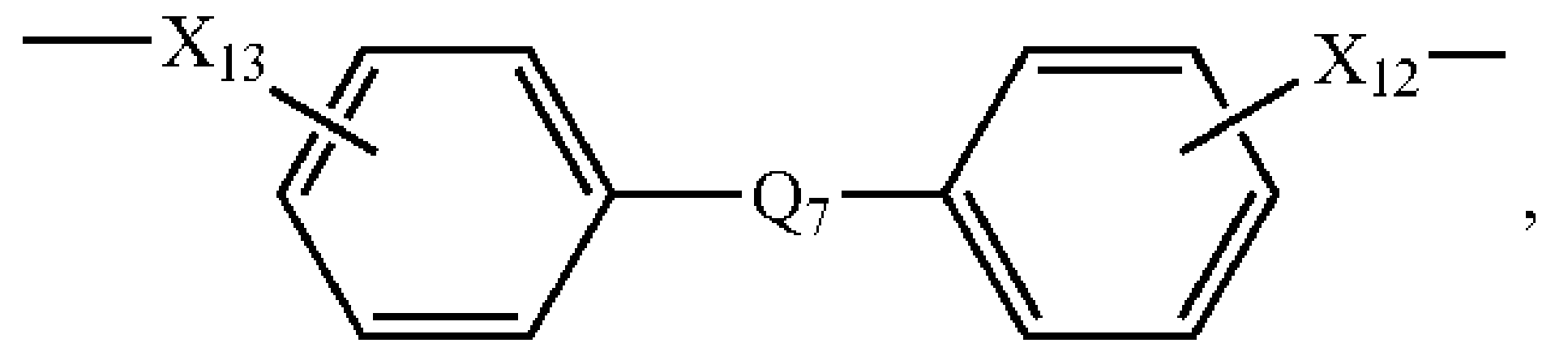
3. An organophotoreceptor according to claim **2** wherein X_3 is selected from the group consisting of the following formulae:





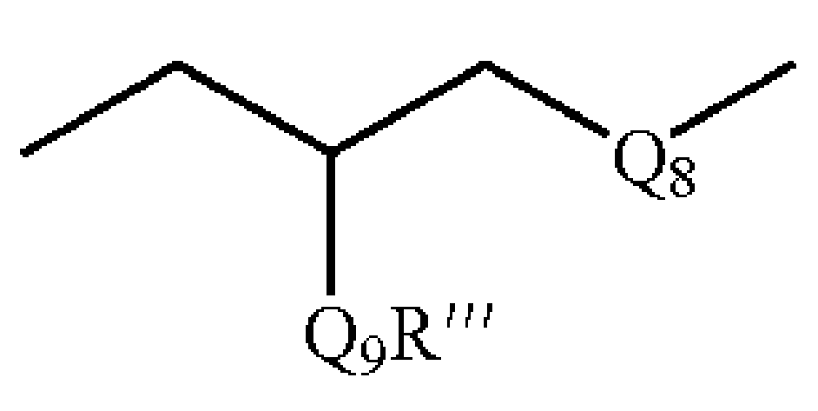






where Q_7 is a bond, O, S, C=O, SO_2, C(=O)O, an NR_b group, or a CR_cR_d group; R_a, R_b, R_c, and R_d are, each independently, H, or an alkyl group; and X_4, X_5, X_6, X_7, X_8, X_9, X_{10}, X_{11}, X_{12}, and X_{13} are, each independently, a bond or a bridging group, such as a —$(CH_2)_p$— group, where p is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, C=O, O=S=O, an aromatic group, an NR_q group, or a CR_sR_t group, where R_q, R_s, and R_t, are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, or an alkoxy group.

4. An organophotoreceptor according to claim **3** wherein X_4, X_5, X_6, X_7, X_8, X_9, X_{10}, X_{11}, X_{12}, and X_{13} have, each independently, the following formula:



where Q_8 and Q_9 are, each independently, O, S, NR'' where R'' and R''' are, each independently, H, or an alkyl group.

5. An organophotoreceptor according to claim **4** wherein Q_2, Q_3, Q_5, and Q_6 are each O.

6. An organophotoreceptor according to claim **1** wherein Q_1 and Q_4 are each S.

7. An organophotoreceptor according to claim **1** wherein R_1 and R_2 comprise, each independently, an aryl group.

8. An organophotoreceptor according to claim **7** wherein X_1 and X_2 are, each independently, a —$(CH_2)_n$— group where n is an integer between 1 and 3.

9. An organophotoreceptor according to claim **1** wherein the photoconductive element further comprises a second charge transport material.

10. An organophotoreceptor according to claim **9** wherein the second charge transport material comprises an electron transport compound.

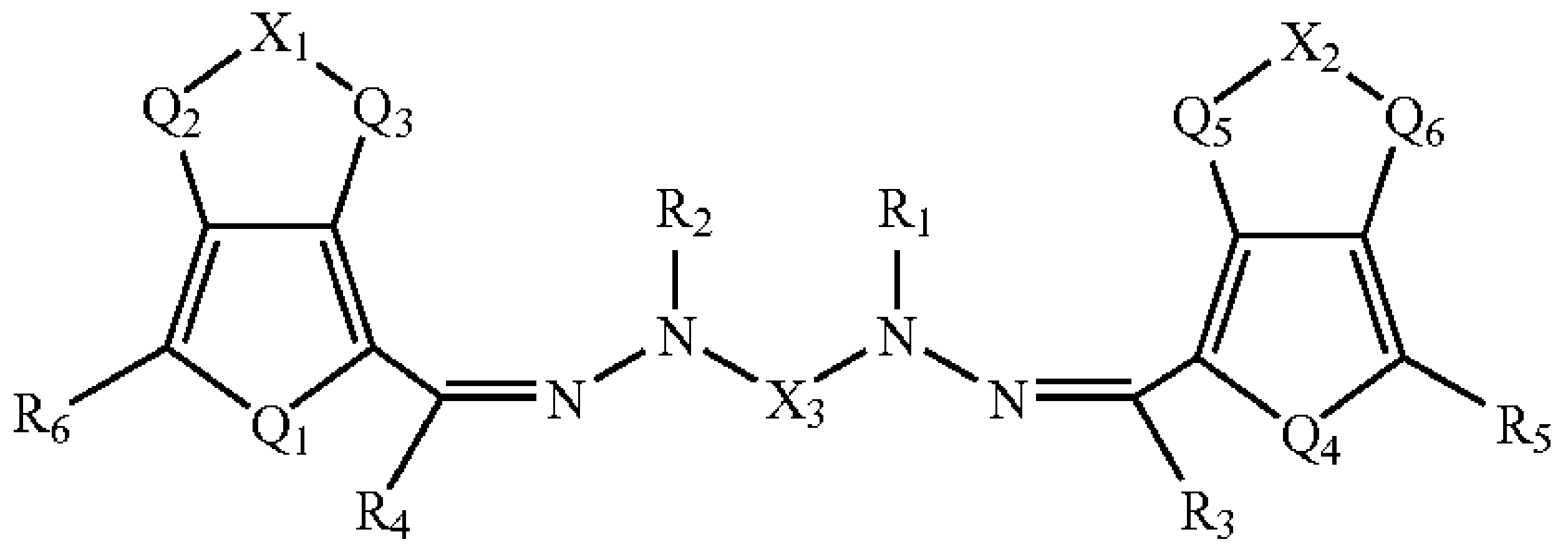
11. An organophotoreceptor according to claim **1** wherein the photoconductive element further comprises a binder.

12. An electrophotographic imaging apparatus comprising:

(a) a light imaging component; and

(b) an organophotoreceptor oriented to receive light from the light imaging component, the organophotoreceptor comprising an electrically conductive substrate and a photoconductive element on the electrically conductive substrate, the photoconductive element comprising:

(i) a charge transport material having the formula



where R_1, R_2, R_3, R_4, R_5, and R_6 comprise, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group;

X_1 and X_2 are, each independently, a —$(CH_2)_n$— group, where n is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, C═O, O═S═O, an NR_a group, or a group, a CR_cR_d group, where R_a, R_c, and R_d, are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, or an alkoxy group;

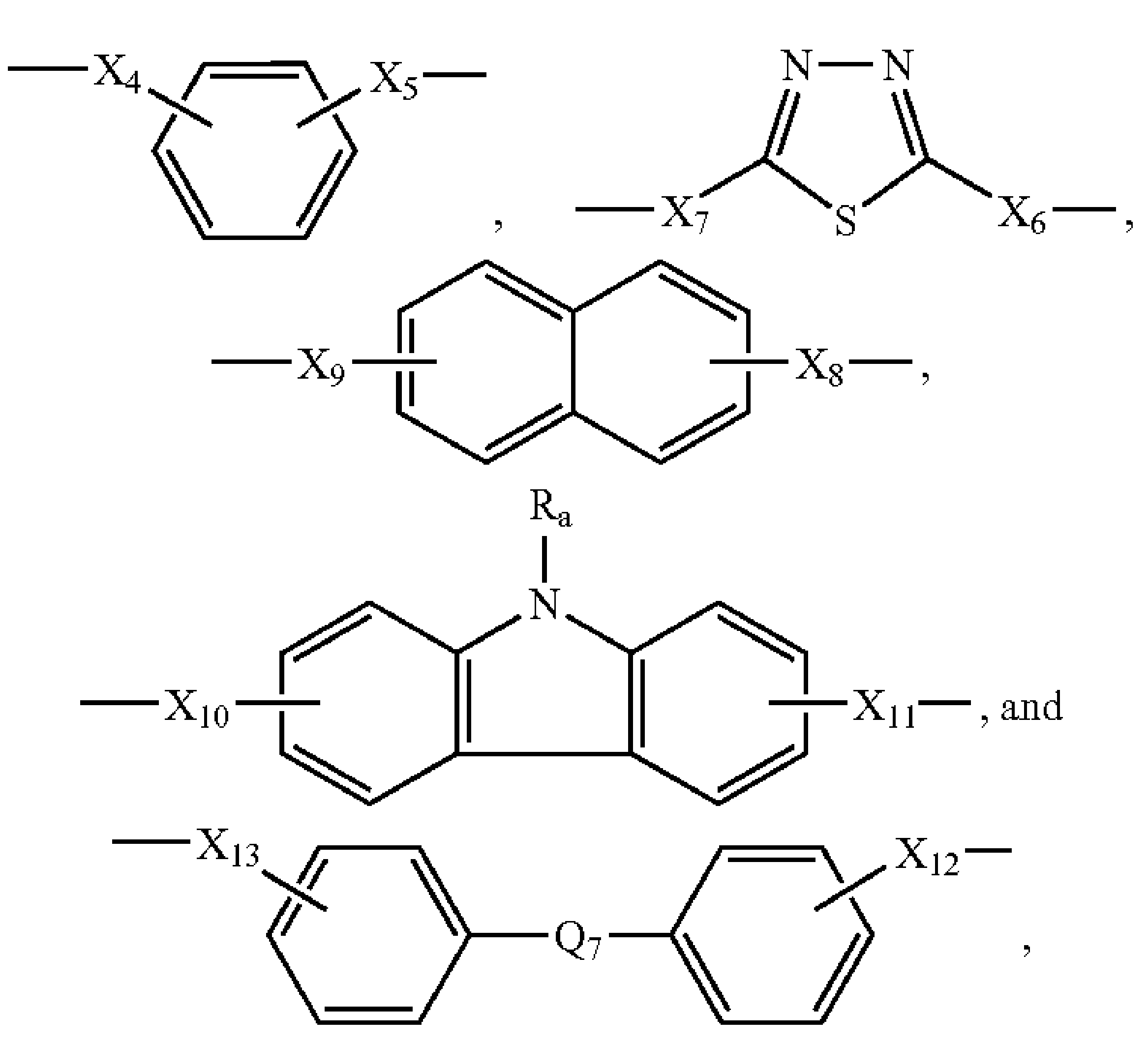
X_3 is linking group; and

Q_1, Q_2, Q_3, Q_4, Q_5, and Q_6 are, each independently, O, S, NR, where R is H, or an alkyl group; and

(ii) a charge generating compound.

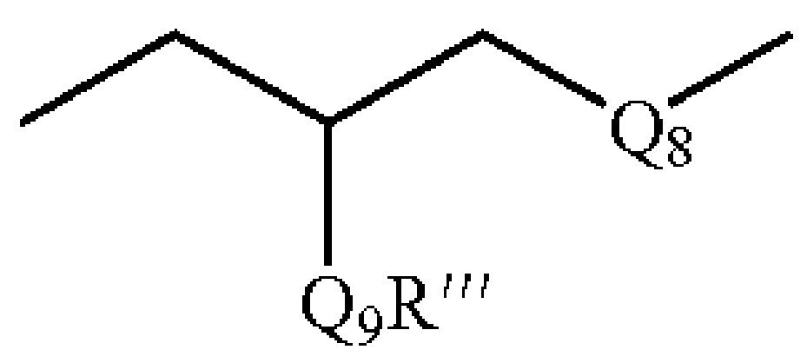
13. An electrophotographic imaging apparatus according to claim **12** wherein X_3 comprises a —$(CH_2)_m$— group, where m is an integer between 1 and 50, inclusive, and one or more of the methylene groups is optionally replaced by O, S, C═O, O═S═O, an aromatic group, an NR_i group, or a CR_kR_l group, where R_i, R_k, and R_l, are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, or an alkoxy group.

14. An electrophotographic imaging apparatus according to claim **13** wherein X_3 is selected from the group consisting of the following formulae:



where Q_7 is a bond, O, S, C═O, SO_2, C(═O)O, an NR_b group, or a CR_cR_d group; R_a, R_b, R_c, and R_d are, each independently, H, or an alkyl group; and X_4, X_5, X_6, X_7, X_8, X_9, X_{10}, X_{11}, X_{12}, and X_{13} are, each independently, a bond or a bridging group, such as a —$(CH_2)_p$— group, where p is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, C═O, O═S═O, an aromatic group, an NR_q group, or a CR_sR_t group, where R_q, R_s, and R_t, are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, or an alkoxy group.

15. An electrophotographic imaging apparatus according to claim **14** wherein X_4, X_5, X_6, X_7, X_8, X_9, X_{10}, X_{11}, X_{12}, and X_{13} have, each independently, the following formula:



where Q_8 and Q_9 are, each independently, O, S, NR'' where R'' and R''' are, each independently, H, or an alkyl group.

16. An electrophotographic imaging apparatus according to claim **15** wherein Q_2, Q_3, Q_5, and Q_6 are each O.

17. An electrophotographic imaging apparatus according to claim **12** wherein Q_1 and Q_4 are each S.

18. An electrophotographic imaging apparatus according to claim **12** wherein R_1 and R_2 comprise, each independently, an aryl group.

19. An electrophotographic imaging apparatus according to claim **18** wherein X_1 and X_2 are, each independently, a —$(CH_2)_n$— group where n is an integer between 1 and 3.

20. An electrophotographic imaging apparatus according to claim **12** wherein the photoconductive element further comprises a second charge transport material.

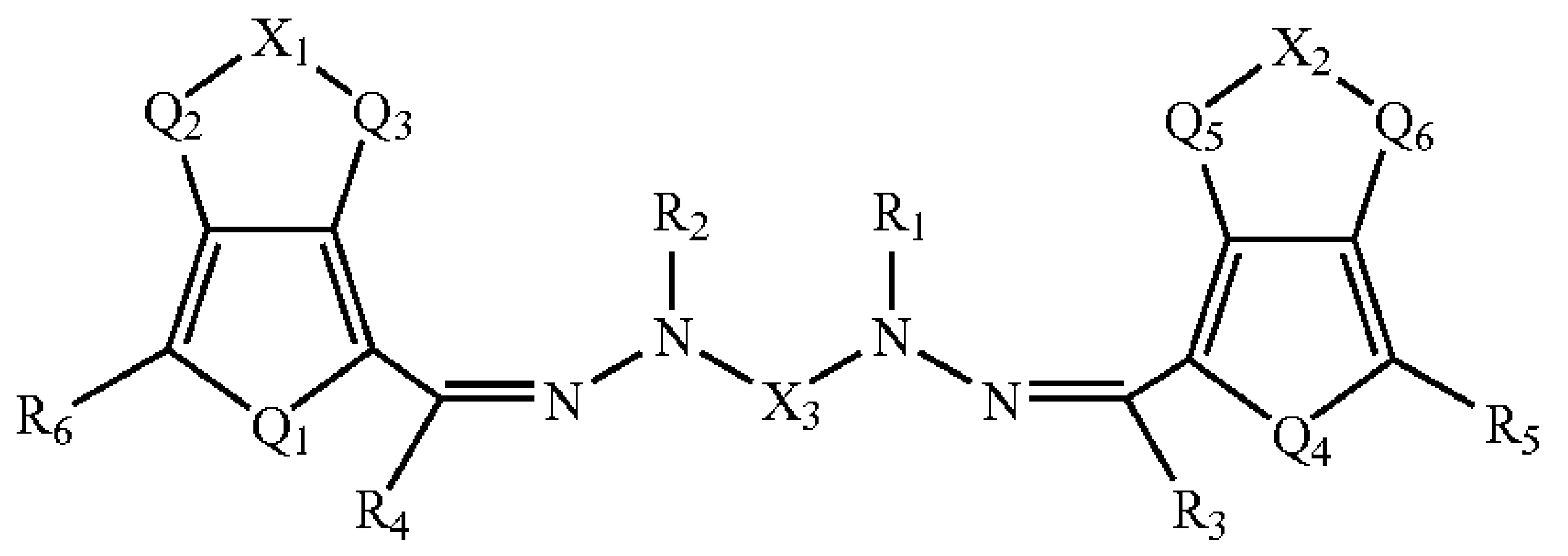
21. An electrophotographic imaging apparatus according to claim **20** wherein second charge transport material comprises an electron transport compound.

22. An electrophotographic imaging apparatus according to claim **12** further comprising a toner dispenser.

23. An electrophotographic imaging process comprising;

(a) applying an electrical charge to a surface of an organophotoreceptor comprising an electrically conductive substrate and a photoconductive element on the electrically conductive substrate, the photoconductive element comprising

(i) a charge transport material having the formula



where R_1, R_2, R_3, R_4, R_5, and R_6 comprise, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group;

X_1 and X_2 are, each independently, a —$(CH_2)_n$— group, where n is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, C═O, O═S═O, an NR_a group, or a CR_cR_d group, where R_a, R_c, and R_d, are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, or an alkoxy group;

X_3 is linking group; and

Q_1, Q_2, Q_3, Q_4, Q_5, and Q_6 are, each independently, O, S, NR, where R is H, or an alkyl group; and

(ii) a charge generating compound

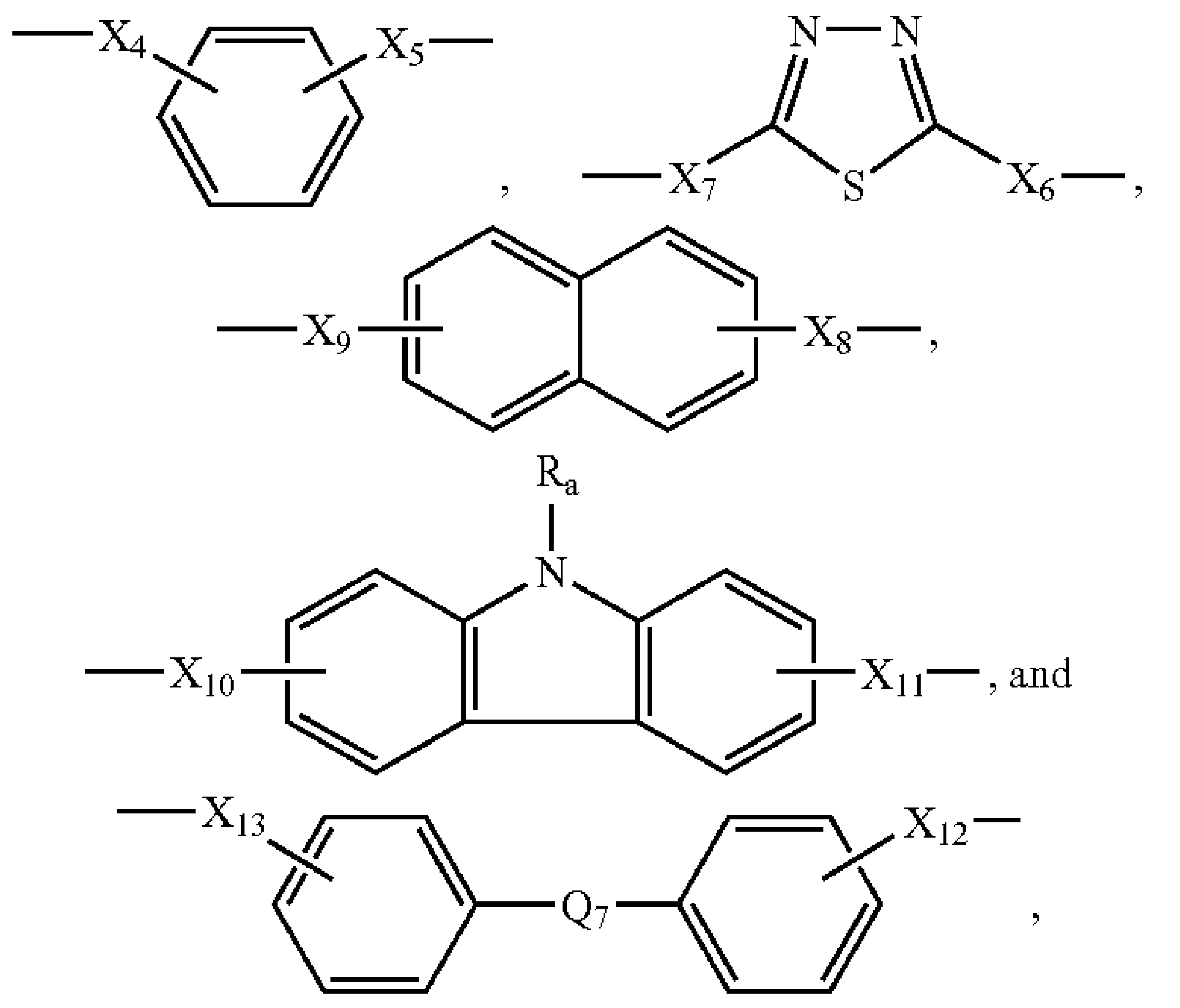
(b) imagewise exposing the surface of the organophotoreceptor to radiation to dissipate charge in selected areas and thereby form a pattern of charged and uncharged areas on the surface;

(c) contacting the surface with a toner to create a toned image; and

(d) transferring the toned image to substrate.

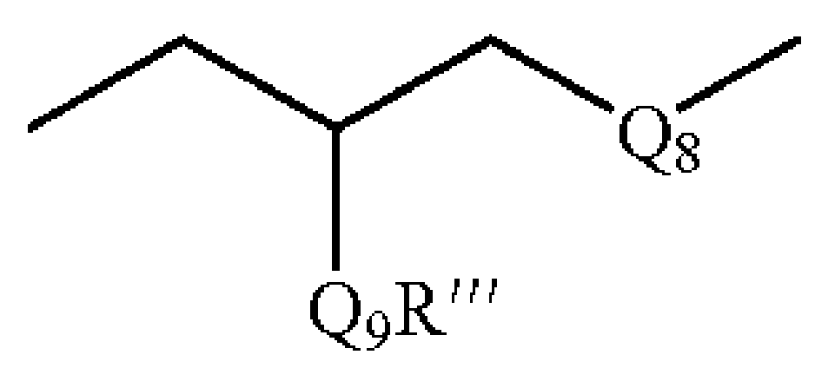
24. An electrophotographic imaging process according to claim **23** wherein X_3 comprises a —$(CH_2)_m$— group, where m is an integer between 1 and 50, inclusive, and one or more of the methylene groups is optionally replaced by O, S, C═O, O═S═O, an aromatic group, an NR_i group, or a CR_kR_l group, where R_i, R_k, and R_l, are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, or an alkoxy group.

25. An electrophotographic imaging process according to claim **24** wherein X_3 is selected from the group consisting of the following formulae:



where Q_7 is a bond, O, S, C=O, SO_2, C(=O)O, an NR_b group, or a CR_cR_d group; R_a, R_b, R_c, and R_d are, each independently, H, an alkyl group; and X_4, X_5, X_6, X_7, X_8, X_9, X_{10}, X_{11}, X_{12}, and X_{13} are, each independently, a bond or a bridging group, such as a $—(CH_2)_p—$ group, where p is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, C=O, O=S=O, a an aromatic group, an NR_q group, or a CR_sR_t group, where R_q, R_s, and R_t, are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, or an alkoxy group.

26. An electrophotographic imaging process according to claim **25** wherein X_4, X_5, X_6, X_7, X_8, X_9, X_{10}, X_{11}, X_{12}, and X_{13} have, each independently, the following formula:



where Q_8 and Q_9 are, each independently, O, S, NR" where R" and R'" are, each independently, H, or an alkyl group.

27. An electrophotographic imaging process according to claim **26** wherein Q_2, Q_3, Q_5, and Q_6 are each O.

28. An electrophotographic imaging process according to claim **23** wherein Q_1 and Q_4 are each S.

29. An organophotoreceptor according to claim **23** wherein R_1 and R_2 comprise, each independently, an aryl group.

30. An organophotoreceptor according to claim **29** wherein X_1 and X_2 are, each independently, a $—(CH_2)_n—$ group where n is an integer between 1 and 3.

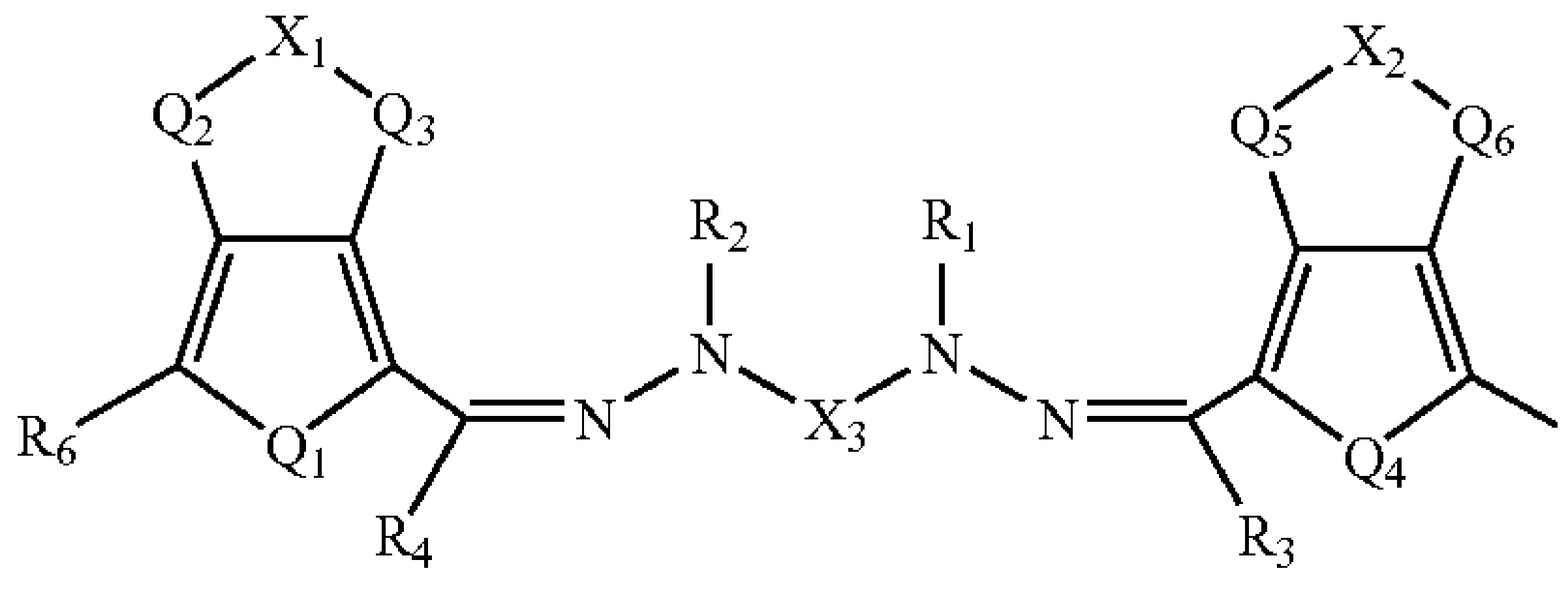
31. An electrophotographic imaging process according to claim **23** wherein the photoconductive element further comprises a second charge transport material.

32. An electrophotographic imaging process according to claim **31** wherein the second charge transport material comprises an electron transport compound.

33. An electrophotographic imaging process according to claim **23** wherein the photoconductive element further comprises a binder.

34. An electrophotographic imaging process according to claim **23** wherein the toner comprises colorant particles.

35. A charge transport material having the formula



where R_1, R_2, R_3, R_4, R_5, and R_6 comprise, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group;

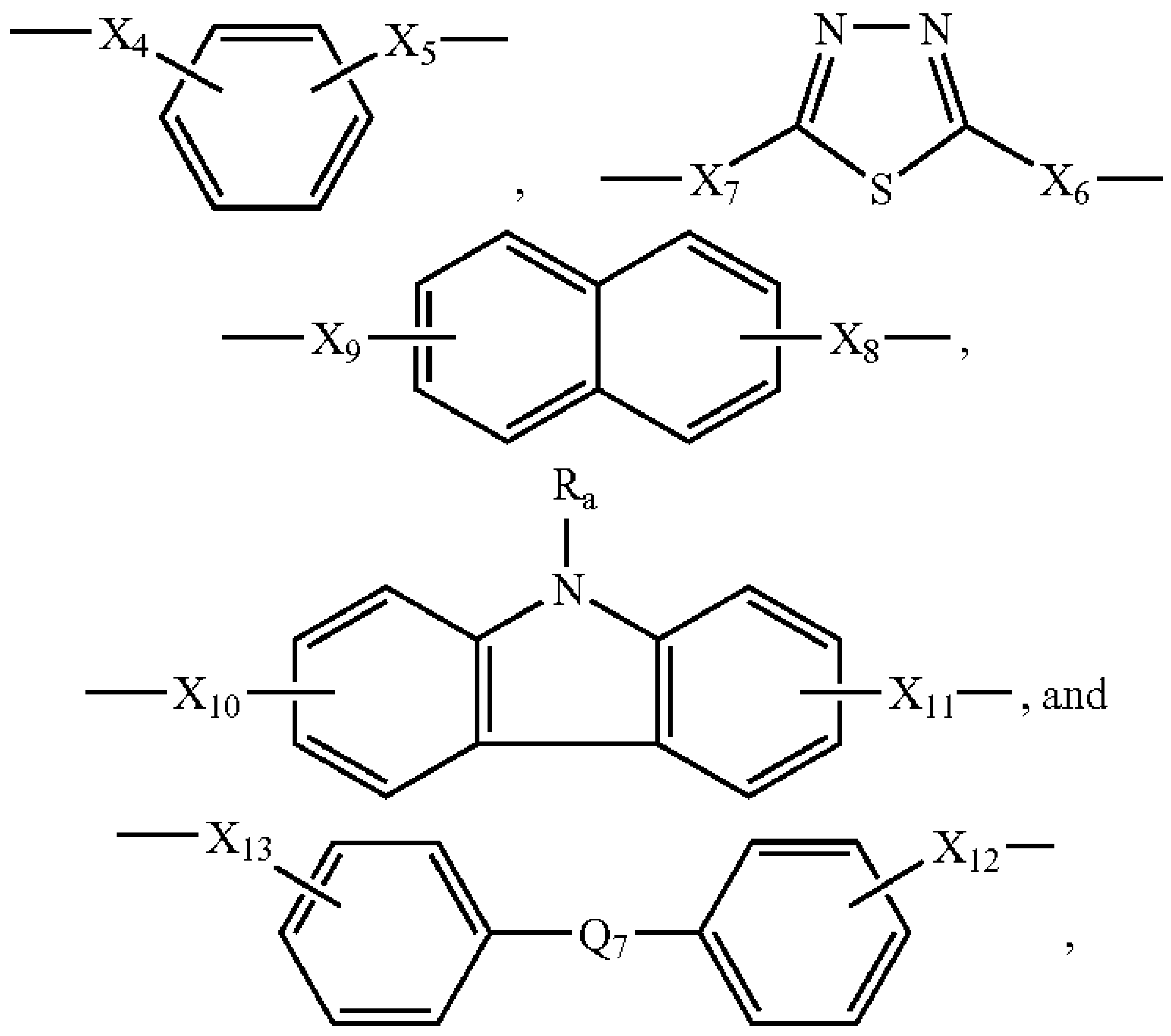
X_1 and X_2 are, each independently, a $—(CH_2)_n—$ group, where n is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, C=O, O=S=O, an NR_a group, or a CR_cR_d group, where R_a, R_c, and R_d, are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, or an alkoxy group;

X_3 is linking group; and

Q_1, Q_2, Q_3, Q_4, Q_5, and Q_6 are each independently, O, S, NR, where R is H, or an alkyl group.

36. A charge transport material according to claim **35** wherein X_3 comprises a $—(CH_2)_m—$ group, where m is an integer between 1 and 50, inclusive, and one or more of the methylene groups is optionally replaced by O, S, C=O, O=S=O, an aromatic group, an NR_i group, or a CR_kR_l group, where R_i, R_k, and R_l, are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, or an alkoxy group.

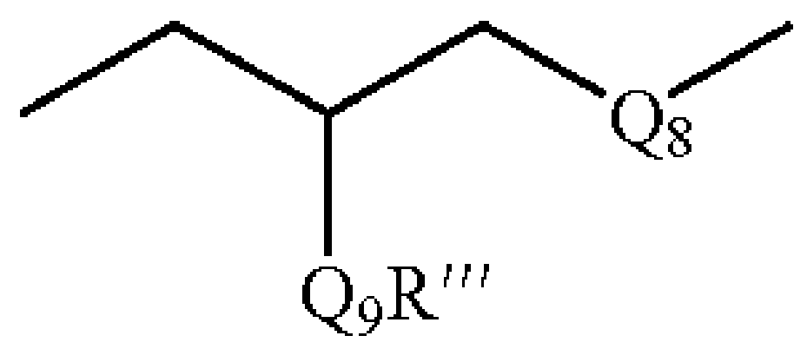
37. A charge transport material according to claim **36** wherein X_3 is selected from the group consisting of the following formulae:



where Q_7 is a bond, O, S, C=O, SO_2, C(=O)O, an NR_b group, or a CR_cR_d group; R_a, R_b, R_c, and R_d are, each independently, H, or an alkyl group; and X_4, X_5, X_6, X_7, X_8, X_9, X_{10}, X_{11}, X_{12}, and X_{13} are, each independently, a bond or a bridging group, such as a

—$(CH_2)_p$— group, where p is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, C═O, O═S═O, an aromatic group, an NR_q group, or a CR_sR_t group, where R_q, R_s, and R_t, are, each independently, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, a halogen, an alkyl group, or an alkoxy group.

38. A charge transport material according to claim **37** wherein X_4, X_5, X_6, X_7, X_8, X_9, X_{10}, X_{11}, X_{12}, and X_{13} have, each independently, the following formula:



where Q_8 and Q_9 are, each independently, O, S, NR'' where R'' and R''' are, each independently, H, or an alkyl group.

39. A charge transport material according to claim **38** wherein Q_2, Q_3, Q_5, and Q_6 are each O.

40. A charge transport material according to claim **35** wherein Q_1 and Q_4 are each S.

41. A charge transport material according to claim **35** wherein R_1 and R_2 comprise, each independently, an aryl group.

42. A charge transport material according to claim **41** wherein X_1 and X_2 are, each independently, a —$(CH_2)_n$— group where n is an integer between 1 and 3.

* * * * *